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Trace Elements of Fly Ash: Emissions from Coal-Fired Steam Plants Equipped with Hot-Side and Cold-Side Electrostatic Precipitators for Particulate Control

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This report describes the results of a sampling and chemical analysis study of emissions from two coal-fired steam plants equipped with electrostatic precipitators for particulate control. The program objective was to define both emission and enrichment of trace elements in the flue gas exiting electrostatic precipitators operated at different process temperatures. Fly ash collected from the stack using cyclones and cascade impactors was analyzed to define trace element concentration of individual size fractions. Trace element enrichment of ash fractions was compared with an enrichment model to define the dependence of enrichment on particle size. Samples of the feed coal at each station were subjected to density separation to determine the association of each element with mineral (ash) and organic (ash-free) phases of the coal. The 15 elements included in the coal and ash studies are:

Arsenic,
Beryllium,
Cadmium,
Calcium,
Chromium,
Copper,
Fluorine,
Lead,
Manganese,
Mercury,
Nickel,
Selenium,
Titanium,
Uranium, and
Zinc

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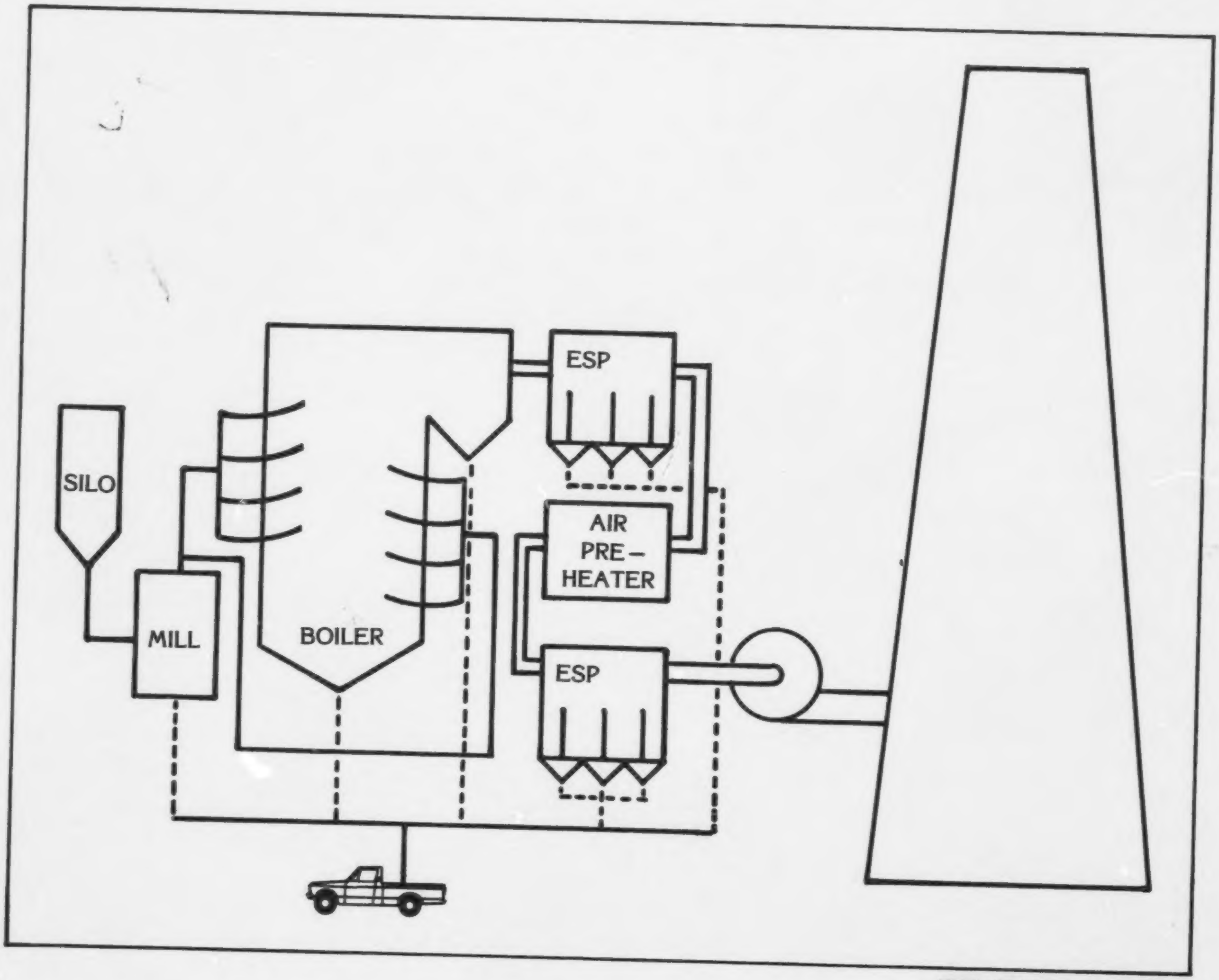

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FINAL REPORT

TRACE ELEMENTS OF FLY ASH: EMISSIONS FROM COAL-FIRED STEAM PLANTS EQUIPPED WITH HOT-SIDE AND COLD-SIDE ELECTROSTATIC PRECIPITATORS FOR PARTICULATE CONTROL

By

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ABSTRACT

This study was sponsored by U. S. Environmental Protection Agency, Region VIII. It describes results obtained by sampling two coal-fired steam plants equipped with electrostatic precipitators (hot-side and cold-side) for particulate control. The field sampling conducted during September 1976 included the following streams:

coal,
fly ash.

The objective of the program was to define both emission and enrichment of trace elements in the flue gas particulates. Particulate loading of the flue gas was determined daily; particle size distribution was determined by Andersen cascade impactor with glass fiber filter substrates. Fly ash was collected using both cyclones and cascade impactors for trace element analysis of individual size fractions.

Samples of the feed coal at each station were subjected to density (sink-float) separation to determine elemental association with the mineral (ash) phase and organic (ash-free) phase.

The 15 elements included in both coal and ash studies are:

Arsenic
Beryllium
Cadmium
Calcium
Chromium
Copper
Fluorine
Lead
Manganese
Mercury
Nickel
Selenium
Titanium
Uranium
Zinc

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1.0 INTRODUCTION

Radian was contracted by EPA to perform a field sampling and analysis program to investigate several aspects of trace element emissions from coal-fired boilers. Specific objectives were to:

- quantify trace element enrichment in fly ash compared to raw coal,
- determine trace element enrichment as a function of particle size,
- investigate affinity of elements for inorganic or organic fractions of coal, and
- investigate particulate collection efficiency and trace element enrichment of emitted fly ash of hot side and cold side electrostatic precipitation control devices.

During September 1976, raw coal and flue gas streams were sampled at two western power plants firing low-sulfur subbituminous coals. One station was equipped with cold-side electrostatic precipitators (ESP) and the other station used hot-side ESP's for particulate control. Grain loading and particle size distribution of the fly ash was determined by sampling the stack at each plant. Fly ash was collected in three size fractions using three high volume cyclones in series and also in eight fractions using an Anderson Mark II cascade impactor as primary collectors. A wet electrostatic precipitator (WEP) was used downstream of both primary collectors to collect species escaping the primary collector. The cyclone and Anderson sized particulate samples and the WEP samples were analyzed for up to 15 trace elements.

Enrichment ratios were calculated for each element; in this study the enrichment ratio was defined as the ratio of the concentration of a given element in the ash fraction to its expected concentration in the coal ash based on analysis of the coal. Physical measurements of selected ash fractions were also performed using scanning electron microscopy and specific surface area techniques. The results of the physical and chemical measurements were examined for possible correlations with the particulate size data and control device.

In addition, the relative distribution of trace elements in the inorganic and organic phases of coal were measured by density separations of finely divided coal and analysis of the fractions. The analytical results for each element were correlated using a least squares technique.

Background

Trace element emissions from coal-fired boilers occur both as fine particulates and volatile matter. Increased interest in fine particulates emitted from coal-fired power plants has resulted from the following findings:

- certain potentially toxic trace elements are preferentially concentrated in the fines,
- fine particulates are not as efficiently retained by conventional control devices as larger sized particulates,

- fine particulates are primarily responsible for visibility degradation since they are in the effective light scattering region,

- slow settling rates for fine particulates result in long transport distances, and

- fine particulates exhibit a high degree of retention in the human respiratory system.

Current EPA emission standards for particulates are based on total mass; however, there is mounting evidence that both size distribution and chemical composition are important factors in human health effects. Of most concern are the particles in the 0.5-2 micron size range, since the retention in the respiratory organs shows a maximum in this area as shown in Figure 1-1 (GO-075). EPRI is currently sponsoring a study of the effects of fly ash particulates on a particular type of lung cell called macrophages; these cells function as an important defense mechanism in the human lung by ingesting foreign materials which enter the lung (RE-295). Other related health effects investigations are aimed at identifying toxic or synergistic effects of trace particulate components such as vanadium and cadmium on respiratory functions.

Several types of investigations of the trace element enrichment phenomenon have recently been carried out to define the mechanisms involved and the degree of concentration taking place. A data base is being established in three areas:

- distribution of trace elements throughout ash and flue gas fractions,

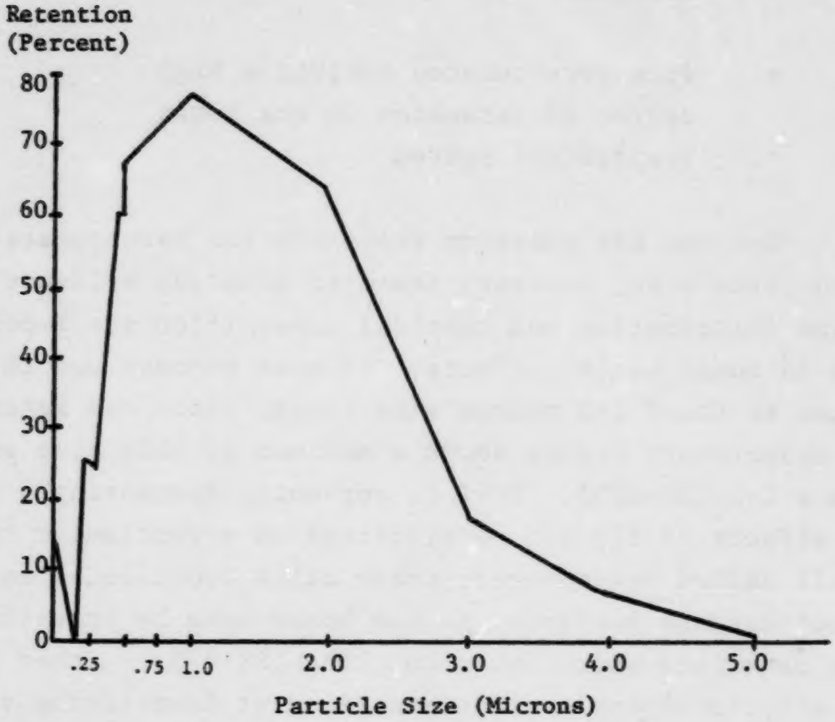

Figure 1-1. Retention of Particulate Matter in Lung in Relation to Particle Size

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Source: GO-075

- mode of occurrence of trace contaminants in fuel, and
- collection efficiency of existing particulate control devices for each element.

The results from these studies will be used to develop a predictive capability for determining trace element emissions and control requirements for individual plants based on coal analysis and boiler and flue gas cleaning system characteristics.

In-depth field studies and trace elements distributions in 10 different coal-fired power plant systems have been reported by Radian and other investigators (KA-192, BO-124, BR-452, CO-342, KL-095, RA-219, LE-289, DA-105, GO-253, and FI-167). Comparison of fly ash analyses with trace element profiles in the corresponding coals shows that some elements are enriched by the coal combustion process. Enrichment is most evident in the smallest fly ash particles. In most studies those elements which were reported to undergo enrichment in the smaller particles of emitted flue gas include:

Antimony
Arsenic
Bromine
Copper
Cadmium
Chromium
Chlorine
Fluorine
Gallium
Iodine
Lead
Mercury
Molybdenum
Selenium
Sulfur
Zinc

Of these 16 elements, mercury, selenium, zinc, bromine, fluorine, sulfur, and chlorine are generally thought to be emitted from the stack either totally or partially as vapors.

Those which were reported approximately equally distributed in all ash fractions include:

Aluminum
Barium
Calcium
Iron
Magnesium
Silicon
Rubidium
Strontium
Tin

There are differences of opinion with regard to some elements. In some studies enrichment tendencies were found, while in other studies no significant enrichment as a function of particle size was reported. This type of disagreement was evident for the following:

Beryllium
Cobalt
Manganese
Titanium
Vanadium

Further evidence of surface concentration of some elements was reported by Linton (TO-087). Using a technique described as "molecular sandblasting," surface concentrations of lead and thallium on coal fly ash particulates were found to be 40,000 and 4,500 ppm, respectively. These surface values are indicative of a surface concentration mechanism when compared to measurements of 620 and 30 ppm lead and thallium in coal fly ash.

The phenomenon of the observed element enrichment can be explained by the volatilization of these elements or their compounds in the fire box of the boiler. This volatilization provides the mechanism for the selective partitioning of elements during the fractionation of the ash between fly ash and bottom ash.

The volatilized elements or their compounds subsequently remain gaseous, condense partially or condense completely.

In the first case, a high percentage of an element incoming with the coal will be discharged through the stack unless flue gas control devices are designed for their collection. Partial or complete condensation will lead to an increase in the concentration in the fine particulate fraction of the fly ash. Condensation can occur by nucleation or deposition on available surfaces. At the relatively low residence times (5-10 seconds) between volatilization and condensation, any nucleation that occurs should result in small particles. Deposition on the fly ash particles will be surface area dependent. This also will result in increased concentrations in the small particulates since the specific surface area is greater for the smaller ash particles.

The form in which a trace element naturally occurs in the coal may be one determinant of its distribution throughout the combustion system. Some workers have speculated that certain metallic elements preferentially associated with the organic phase of coal are released during combustion as very fine particles of metal oxides. Several studies to identify tendencies of elements to associate with either the mineral (inorganic) or organic phase of coal have been reported (GL-077, RU-039, ME-150, ZU-019, HO-417, NI-095 and GO-252). The general findings as summarized in Table 1-1 indicate good agreement among the studies for several elements. Many elements, however, have been found to be associated with the organic phase in one coal and the inorganic phase in another coal. Sometimes no clear cut or preferential phase association is observed. The phase association can vary within a coal seam. Variations can depend on mineral and sulfur content which are directly effected by coal type and formation circumstances.

TABLE 1-1. SUMMARIZED ELEMENT AFFINITY STUDIES

Predominantly Organic Affinity	Organic & Inorganic Associations	Predominantly Inorganic Affinity
Br	Ca	As
B	Cr	Ba
Be	Cu	Cd
Ga	Co	Fe
Ge	Cs	Hg
Ti	Mo	La
Sb	Ni	Mn
	V	P
	Y	Pb
	Se	Sn
	U	Sr
		Zn

F - Not reported in literature.

Element enrichment through the volatilization mechanism may have a pronounced impact on the selection of particulate removal devices. The particulate collector most widely used in the utility industry is the cold-side electrostatic precipitator operating near 250°F. This collector has been operated near 700°F as a hot-side precipitator (HS ESP) in some existing stations and is being considered for new generating stations burning Western low-sulfur coal. The hot-side precipitator has been found to be a more efficient particulate removal device due to the lower resistivity of this type of coal ash at higher temperatures. The use of the hot-side precipitator has been theorized to be of questionable environmental assistance. If higher volatile trace element emissions due to incomplete recondensation at higher operating temperatures of the precipitator are observed, the increased particulate removal capabilities might be offset. This study was designed to compare the emitted ash from two electrostatic precipitators operating at different temperatures.

2.0 CONCLUSIONS

The occurrence and distribution of trace elements in fine particulate emissions of two coal-fired generating stations, one equipped with hot-side and one with cold-side electrostatic precipitators, has been investigated in this study. Also the association of trace elements with the organic (ash-free) phase has been determined for the feed coal at each station. The findings of this study are summarized in this section.

2.1 Enrichment of Trace Elements in Fly Ash

Higher average enrichment of the cold-side station fly ash was found for ten of the thirteen elements analyzed in ash samples size fractionated by cyclone collection. Two elements exhibited higher enrichment in the fly ash at the hot-side station.

HIGHEST ENRICHMENT

Hot-Side Station	Cold-Side Station	
Arsenic	Beryllium	Manganese
Selenium	Cadmium	Nickel
	Chromium	Uranium
	Copper	Zinc
	Fluorine	
	Mercury	

No enrichment was observed for the following elements:

Hot-Side Station		Cold-Side Station
Beryllium	Manganese	Titanium
Cadmium	Titanium	
Chromium	Uranium	

2.2 Trace Element Emissions

Higher trace element mass emissions were found at the hot-side ESP station for nine of the thirteen elements for cyclone collected ash. The higher emissions are at least partly the result of precipitator efficiency resulting in a higher particulate loading of the flue gas at the Station HS during the sampling period and are not necessarily the result of precipitator location.

GREATER MASS EMISSIONS

Hot-Side Station		Cold-Side Station
Aresenic	Nickel	Copper
Beryllium	Selenium	Fluorine
Cadmium	Titanium	Mercury
Chromium	Uranium	Zinc
Manganese		

2.3 Estimated Volatile Emissions

Seven of the eight elements included in the cascade impactor collected ash fraction study were estimated to be more volatile under the conditions at the hot-side station. Volatile trace elements were determined indirectly. A separate sample fraction was not collected for volatiles, however an estimation was made of volatiles collected by a wet electrostatic precipitator (WEP). A comparison of the increased enrichment observed in the WEP (vapor and fine particulate) fraction with the enrichment predicted for that fraction from the enrichment versus particle size correlation provided an estimate of volatile emissions. The possibility of homogeneous nucleation of fine particulate matter could not be evaluated or discerned in the study.

HIGHER ESTIMATED VOLATILE EMISSIONS

Hot-Side Station		Cold-Side Station
Arsenic	Nickel	Cadmium
Copper	Selenium	
Chromium	Zinc	
Manganese		

2.4 Correlation of Enrichment with Particle Size

A good correlation of enrichment of fly ash with decreasing particle size was observed at each plant for four common elements:

Arsenic Nickel
Copper Zinc

Three additional elements exhibited this correlation only at the cold-side station:

Cadmium Chromium Manganese

Selenium also exhibited a good correlation of enrichment with particle size but only at the hot-side station.

2.5 Phase Association of Trace Elements in the Coal

Although similar in trace element content, the two feed coals differed in the association of elements with the organic phase.

Elements predominantly associated with the organic phase of both feed coals include:

Beryllium
Calcium
Chromium
Manganese
Nickel
Uranium

Fluorine did not exhibit a phase preference in either coal. Selenium and titanium were inorganically associated in the hot-side coal and exhibited weak to moderate organic association in the cold-side coal.

Arsenic, cadmium, lead, mercury, and zinc were completely associated with the inorganic (mineral) phase of the hot-side coal, while the association ranged from non-preferention to inorganic cold-side coal.

2.6 General Conclusions

The enrichment mechanism of volatilization followed by condensation which was presented in Section 1.0 would predict that the results of a comparison of enrichment between a hot-side and a cold-side ESP would be dependent on the following factors:

- particulate loading at the point of condensation, and
- degree of element volatilization.

2.6.1 Particulate Loading at the Point of Condensation

Particulate loading at the point of condensation determines the available mass upon which condensation can occur.

A higher particulate loading of the gas at that point can dilute enrichment by increasing the mass and therefore spreading the surface condensed contribution over an increased available surface area.

Particulate loading at the point of condensation is dependent on the location of that point between the boiler and the stack. Specific areas have different criteria that directly affect the loading:

- upstream of ESP
  - boiler configuration
  - ash content of coal

- downstream of ESP
  - particulate loading of inlet gas to ESP
  - ESP collection efficiency

For this study stations were chosen to minimize the effect of conditions prior to the ESP. Two stations with similar boiler configuration and feed coal were identified. The coals although similar in type, exhibit different ash content. The increased ash content of the cold-side coal provided a higher particulate loading for the flue gas prior to the ESP.

Particulate loading beyond the ESP is a function of both the collection efficiency of the ESP and the inlet flue gas loading. Although designed for high removal efficiency capabilities, the ESP requires periodic maintenance to continually perform. Neither unit was operating at maximum efficiency during the sampling period.

The point of condensation is also temperature dependent for each element. The chemical form or species of an element when vaporized and any possible alteration upon cooling defines the temperature at which condensation will occur.

Assuming a volatile element condenses during the temperature drop at the air preheater (as temperature decreases from 700° to 250°F), the fly ash exiting the hot-side ESP would be expected to exhibit a higher enrichment. This condition results from a lower particulate loading at the point of condensation. Both arsenic and selenium exhibited higher enrichment in the hot-side fly ash.

2.6.2 Degree of Element Volatilization

The degree of element volatilization is a function of:

- characteristics of the element, and
- association in the coal.

An element such as mercury with a low boiling point is volatilized at fairly low temperatures. Other elements such as iron or nickel are susceptible to forming volatile metal carbonyls in gas streams rich in carbon monoxide. Arsenic, cadmium, chromium, lead, nickel, selenium and zinc exhibit boiling points either as the element or as a compound which would result in partial volatilization in the boiler.

The association of these and other elements in the coal also defines the degree of volatilization possible. Recent results presented by Kuhn (KU-175) indicate the mobility (volatility) of elements during coal pyrolysis is related to the degree of their organic association. This condition was observed in the present study. Higher enrichment for the following elements in fly ash was associated with higher organic phase association in the coal at the cold-side station indicating phase association may influence volatilization:

Beryllium	Chromium	Fluorine	Uranium
Cadmium	Copper	Mercury	Zinc

Although a relationship of enrichment with organic phase association appears, a larger data base including coal and size fractionated fly ash from additional stations is required to substantiate a valid correlation.

2.7 Recommendations for Future Studies

Further investigation is necessary to document the criteria controlling enrichment mechanisms for each element. Important criteria to be considered in an enrichment mechanism study should include:

- use of a common coal when comparing two plants or collection devices,
- operation of each collection device at maximum efficiency, or in a two station study at approximately equal efficiencies and equal flue gas particulate loading,
- collection of several fine particulate fractions (in range of .4 to .1 μm) with a system to allow their separation from vapor phase,
- sampling of flue gas at several points of differing particulate loading and temperature between the boiler and the stack,

- investigation of new fly ash sampling techniques to allow larger quantities of fly ash to be obtained within shorter sampling periods, and

- evaluation of phase association of trace elements in the feed coal at additional plants to build a data base for comparison with fly ash enrichment.

3.0 FIELD SAMPLING

Field sampling of two coal-fired power plants was conducted in September 1976 to define the occurrence and distribution of trace elements as a function of particle size in the fly ash emitted from the units. Descriptions of the two facilities are provided in Section 3.1, while the techniques used to collect the coal and fly ash samples are discussed in the next section. Further details of this aspect of the program are provided in Appendix A which includes a description of each plant, plant operation during sampling, sample points, sampling schedule and techniques utilized.

3.1 Site Description

The two facilities selected have tangentially-fired boiler configurations and are both fueled with Wyoming sub-bituminous coals. They differ in the placement of their electrostatic precipitators (ESP) relative to the combustion air preheaters. Station HS has "hot-side" ESP's; that is, the precipitators are upstream of the air preheater. Station CS has the ESP's positioned downstream of the combustion air preheater; this configuration is termed "cold-side" ESP's.

3.1.1 Hot-Side ESP Station (HS)

The hot-side ESP station consists of two 350 MW tangentially fired boilers. The newer of the two units, Unit 2, was sampled. Hot-side electrostatic precipitators upstream of the combustion air preheaters, designed for 350 MW at an inlet gas temperature of 830°F, are used for fly ash control. The boiler is fired with sub-bituminous coal transported by rail from Wyoming, where it is strip mined. The coal typically contains 30% moisture, 5% ash and 0.5% sulfur and has a heating value of 8400 Btu/lb. The coal is initially stored in open piles from which it is conveyed to five storage silos. Coal from the silos is fed to the mills where it is pulverized prior to delivery to the boiler through a pneumatic conveying system.

Pyrites from the mills, economizer ash and bottom ash are sluiced alternately to an ash pond at approximately 4-hour intervals. The ash collected in the electrostatic precipitators is tranferred to an ash storage silo by a pneumatic conveyor system and removed from the plant site by truck. Flue gas exits the system through a 500-foot stack, approximately 25 feet in diameter.

A schematic of the station with the process streams indicated is presented in Figure 3-1. A listing of flow rates of process streams is provided in Table 3-1.

3.1.2 Cold-Side ESP Station (CS)

Station CS consists of four 500 MW boilers. Unit 1 was sampled in this program. The plant design has electrostatic precipitators located downstream of the combustion air preheaters, hence the term cold-side precipitator. Each boiler is fired with sub-bituminous coal which is mined near the plant and shipped by truck to the plant site. The coal has an average heat content of 9700 Btu/lb and contains approximately 19% moisture, 10% ash and 0.6% sulfur. The coal trucked into the plant is initially stored in piles at the plant site. Storage silos are filled from these piles by conveyor. The coal from the silos is then fed to mills where it is pulverized and then pneumatically conveyed to the boiler.

Approximately three times per shift pyrites from the coal mills, economizer ash and bottom ash are simultaneously

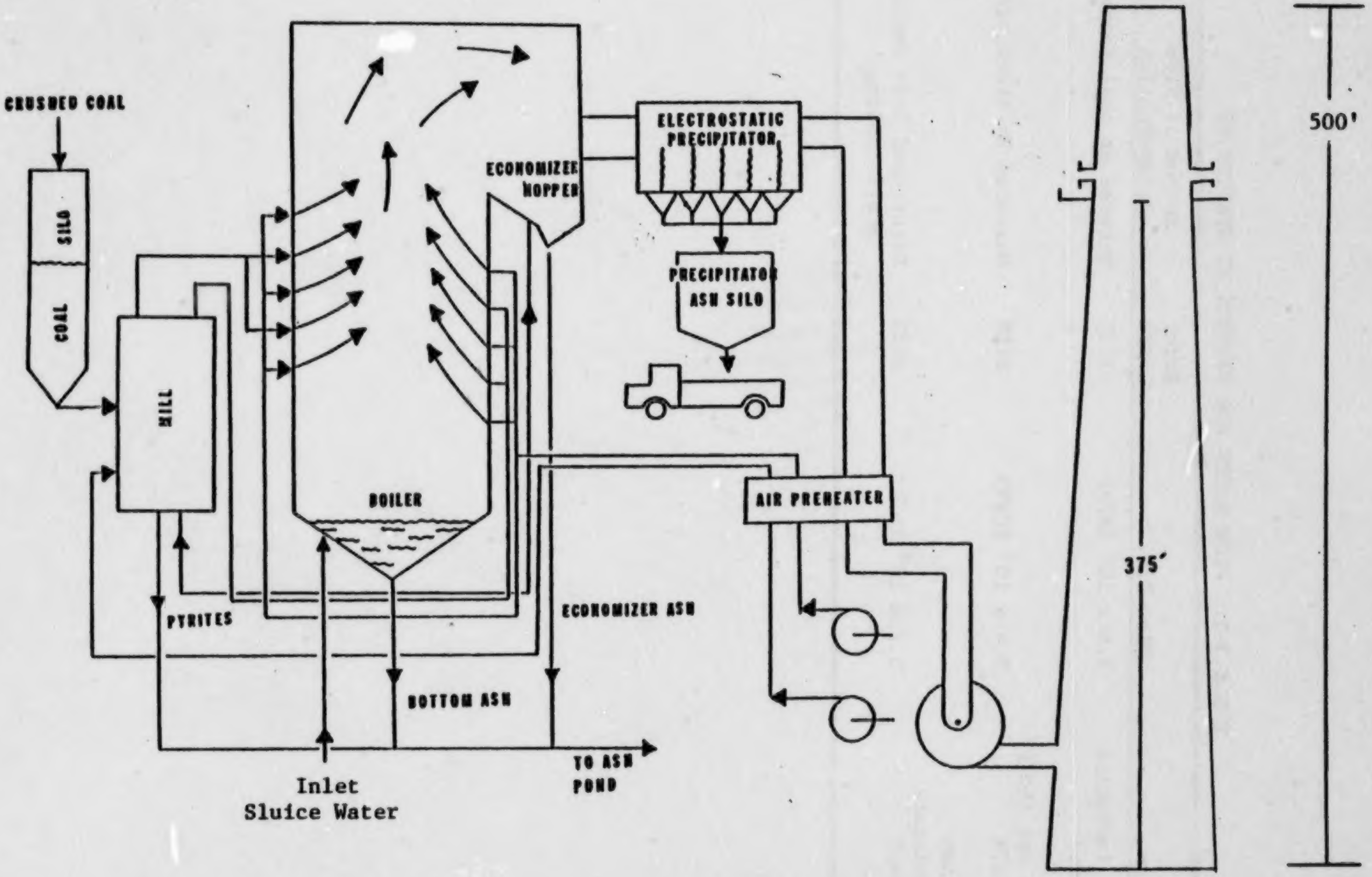

CRUSHED COAL
SILO
COAL
MILL
PYRITES
BOILER
ECONOMIZER HOPPER
ELECTROSTATIC PRECIPITATOR
PRECIPITATOR ASH SILO
AIR PREHEATER
ECONOMIZER ASH
BOTTOM ASH
TO ASH POND
Inlet Sluice Water
375'
500'

Figure 3-1. Schematic of Station HS with Hot-Side Electrostatic Precipitator

TABLE 3-1. FLOW RATES FOR STREAMS AT STATION HS

Stream	Flow Rate	Error Limit	Method of Flow Determination
Coal (moisture free)	2.6×10^5 lb/hr	±10%	Metered at coal feeders
Flue Gas (60^oF/ 1 ATM	5.4×10^7 SCFHD	±10%	Measured by stack traverses
Fly Ash (moisture free)	5.2×10^2 lb/hr	±10%	Determined from cumulative grain loadings

sluiced to a dewatering system. Ash collected in the electrostatic precipitator is pneumatically conveyed to a storage silo from which the ash is taken from the plant site by truck. Flue gas exits the plant through a 500-foot stack which is approximately 24 feet in diameter.

A schematic of the station showing process streams is presented in Figure 3-2. Flow rates of process streams at Station CS are found in Table 3-2.

3.2 Sampling Procedures

The procedures used to sample Stations HS and CS are presented briefly in this section. Details are given in depth in Appendix A, "Sampling". Sampling was performed during the following periods:

- Station HS - September 2-16, 1976 and
- Station CS - September 20-October 1, 1976.

3.2.1 Sampling Points

During the two sampling efforts daily samples of the following materials were collected at the plant sites:

- coal grab samples were collected sequentially at the coal feeders, and
- fly ash samples were collected from the flue gas in the 500-foot stacks.

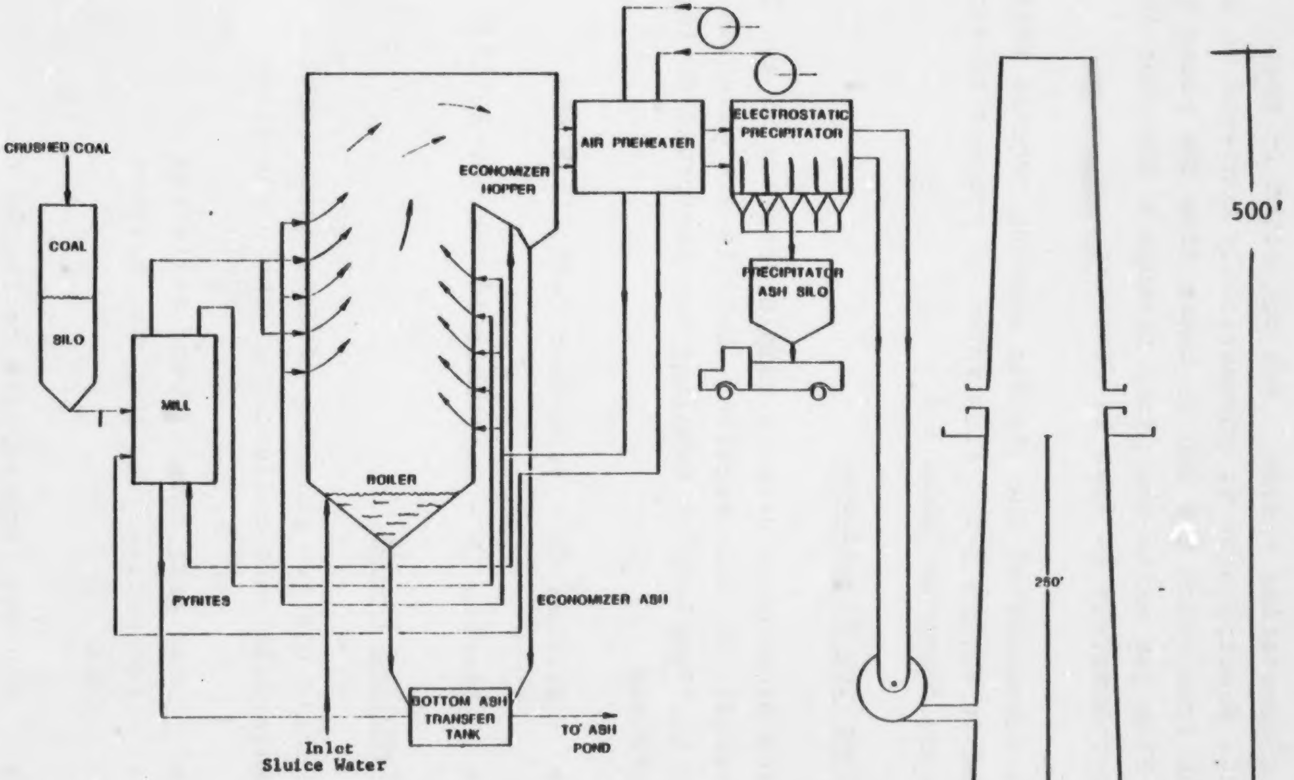

CRUSHED COAL
COAL
SILO
MILL
PYRITES
BOILER
ECONOMIZER HOPPER
Inlet Sluice Water
BOTTOM ASH TRANSFER TANK
TO ASH POND
ECONOMIZER ASH
AIR PREHEATER
ELECTROSTATIC PRECIPITATOR
PRECIPITATOR ASH SILO
250'
500'

Figure 3-2. Schematic of Station CS with Cold-Side Electrostatic Precipitator

TABLE 3-2. FLOW RATES FOR STREAMS AT STATION CS

Stream	Flow Rate	Error Limit	Method of Flow Determination
Coal (moisture free)	4.3 x 10^5 lb/hr	±10%	Metered at coal feeder
Flue gas (60°F/1 ATM)	6.4 x 10^7 SCFHD	±10%	Measured by stack traverses
Fly ash (moisture free)	1.28 x 10^2 lb/hr	±10%	Determined from cumulative grain loadings

Velocity measurements were taken daily at each plant to determine the isokinetic sampling rate and the total gas flow through the stack. The average particulate loading of the flue gas was determined with in-stack Gelman filters. Both flue gas velocity and particulate loading measurements were averaged over the stack area.

Particulate size distribution of the fly ash was determined by an in-stack Andersen cascade impactor. In this device the ash passes through a series of multi-jet stages and is aerodynamically separated and collected on eight plates and a back-up filter. Figures 3-3 and 3-4 present the average fly ash size distributions at Stations HS and CS, respectively.

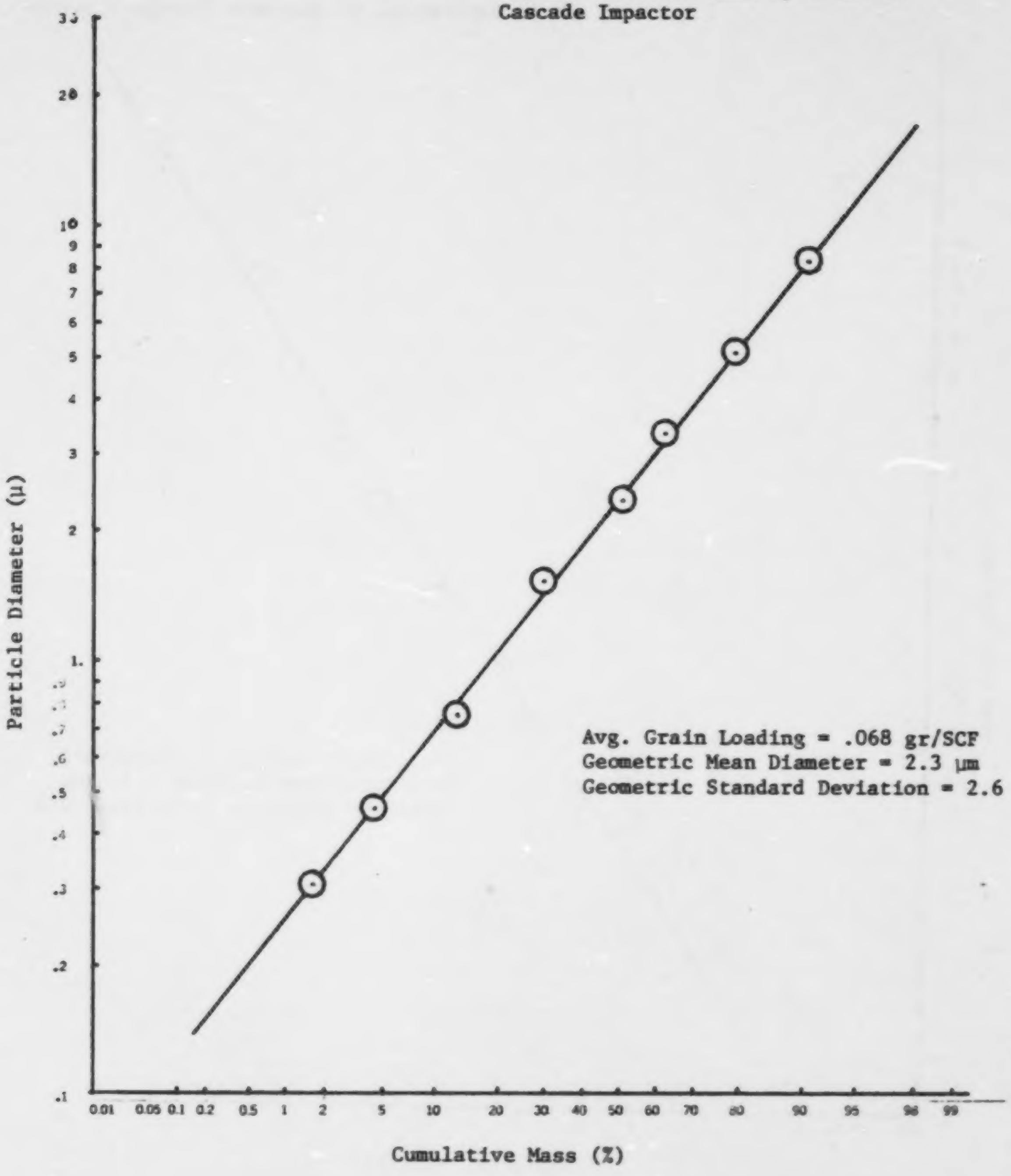
3.3 Fly Ash Collection for Analysis

Fly ash was collected for elemental analysis at each plant by three different methods:

- High-Volume Source Assessment Sampling System (HVSASS) cyclones,
- low volume cyclones, and
- Andersen cascade impactor.

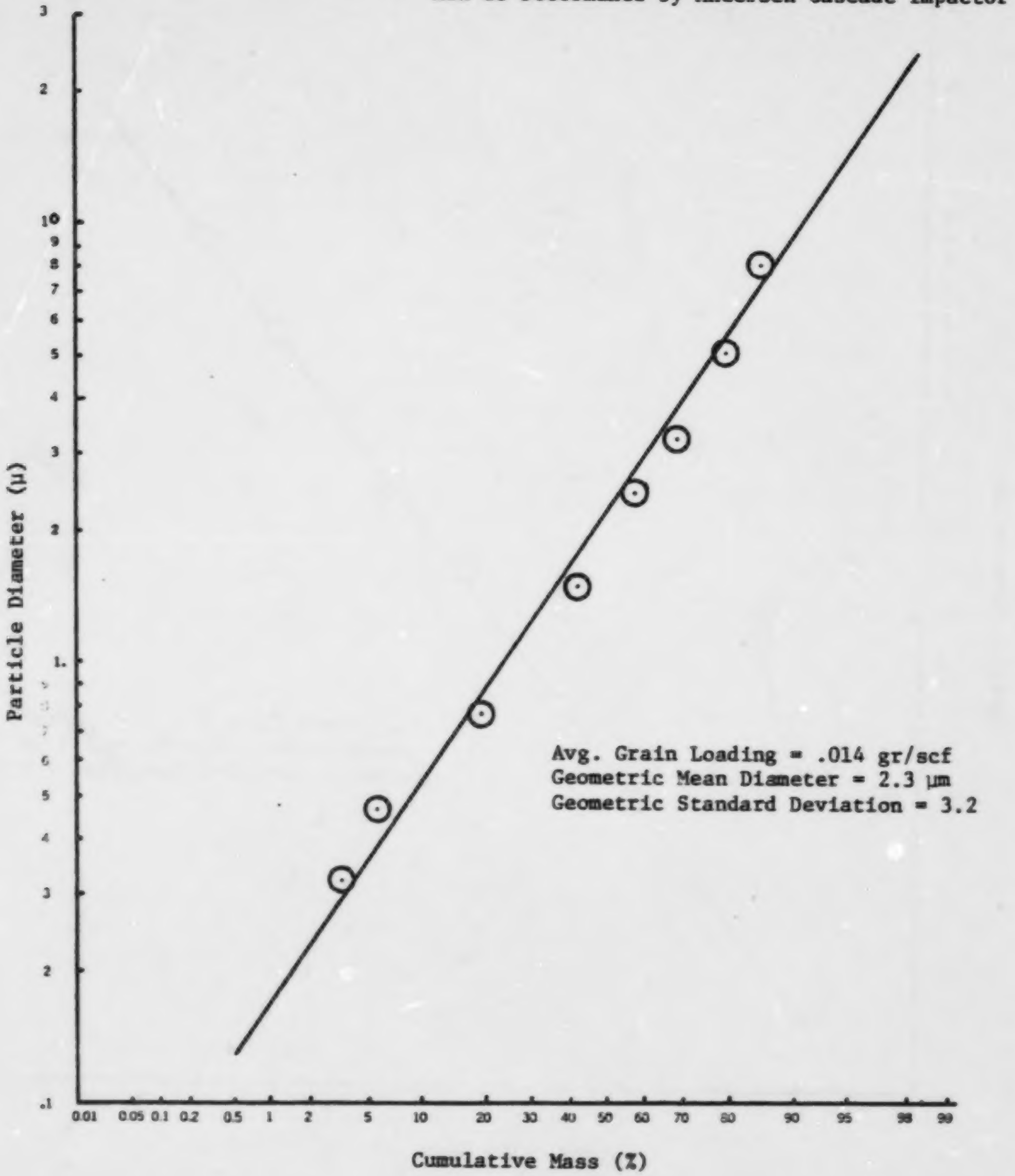
Each of these collection systems was followed by a wet electrostatic precipitator to collect the smallest fraction and vapor species escaping the primary collector. The WEP is >99% effective in removing particulate matter and >95% efficient for most vapor phase trace elements. The only exception in this study was mercury which was sampled in the gas phase by gold amalgamation as an alternate technique. Chemical analysis was carried out on the HVSASS and Andersen samples; the low-volume cyclone samples were held in reserve.

Figure 3-3. Particle Size Distribution of Station HS Fly Ash as Determined by Andersen Cascade Impactor



Avg. Grain Loading = .068 gr/SCF
Geometric Mean Diameter = 2.3 µm
Geometric Standard Deviation = 2.6

Figure 3-4. Particle Size Distribution of Station CS Fly Ash as Determined by Andersen Cascade Impactor



Avg. Grain Loading = .014 gr/scf
Geometric Mean Diameter = 2.3 µm
Geometric Standard Deviation = 3.2

3.3.1 HVSASS Cyclones

The High-Volume Source Assessment Sampling System cyclones are part of a system for source sampling developed by Aerotherm, Inc. under contract to EPA. The system consists of three cyclones designed for a 5ACFM sampling rate. The D_{50}'s (diameter at which 50% of particles are collected) of the cyclone set at the 5ACFM rate are 14 μm, 4 μm and 1 μm. The sampling system as modified for this study is schematically represented in Figure 3-5. Fly ash fractions resulting from HVSASS cyclone collection at isokinetic sampling conditions were analyzed for the 15 trace elements shown below:

- Arsenic
- Beryllium
- Cadmium
- Calcium
- Chromium
- Copper
- Fluorine
- Lead
- Mercury
- Manganese
- Nickel
- Selenium
- Titanium
- Uranium
- Zinc

3.3.2 Low-Volume Cyclones

A series of three cyclones were used to isokinetically collect sized fly ash fractions at 1 ACFM. The cyclones were designed with D_{50}'s of 2.65 μm, 0.96 μm at 1 ACFM. The cyclone system is similar to the HVSASS set except that they are operated in-stack. The 1 ACFM cyclones were manufactured by Radian from specifications provided by Southern Research Institute in Birmingham, Alabama. Both high and low volume cyclone systems were followed by a wet electrostatic precipitator to collect the vaporous and fine particulate material escaping the last cyclone. The low volume cyclone collected ash fractions were held as reserve samples.

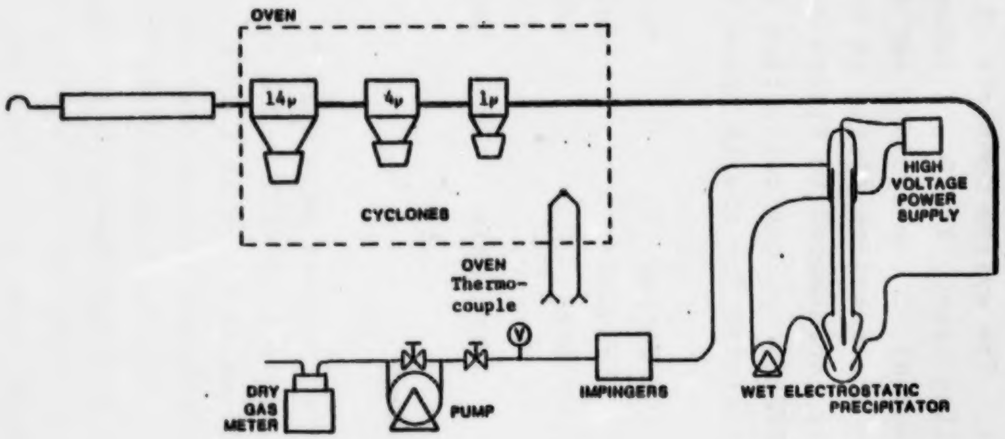

OVEN
14μ
4μ
1μ
CYCLONES
OVEN
Thermo-
couple
HIGH
VOLTAGE
POWER
SUPPLY
DRY
GAS
METER
PUMP
V
IMPINGERS
WET ELECTROSTATIC
PRECIPITATOR

Figure 3-5. Schematic of Sampling Train for Particulate Sizing with HVSASS Cyclones

3.3.3 Cascade Impactor

Particulates entrained in the flue gas were separated during isokinetic sample acquisition into eight size fractions with the Andersen cascade impactor. The Andersen aerodynamically separates the particles as they pass through a series of multi-jet stages. Fine particulates passing through the last impactor stage enter the wet electrostatic precipitator via a teflon-lined probe. Andersen ash fractions were analyzed for the nine trace elements shown below:

Arsenic
Cadmium
Chromium
Copper
Lead
Manganese
Nickel
Selenium
Zinc

3.3.4 WEP Collector

In each sampling train, the wet electrostatic precipitator (WEP) served as the secondary collector of fine particulates escaping the primary collection device. This method permits sampling a large gas volume at isokinetic conditions without plugging, which occurs with a filter. Thus, a sufficient quantity of sample can be collected to permit repeated analyses with low detectability. In addition, problems of trace element contamination by the filter substrate are avoided.

The particulate concentration in the WEP samples was estimated from the titanium concentration assuming that titanium is evenly distributed in the particles with respect to particle size. This assumption is based on work performed by Radian (RA-219) and Davison (DA-105). The results of these two studies indicate that the assumption of uniform ash composition with respect to titanium holds within experimental limits.

The particulate concentration estimated for each WEP sample was subsequently used to determine the concentration of each element in the WEP fraction, reported as mass of element per mass of particulate collected. This is carried out for each element of interest in the WEP sample, regardless of its physical state when collected, i.e., particulate or vapor.

4.0 SAMPLE ANALYSIS

Samples of coal and fly ash collected at each site were analyzed for up to 15 elements:

Arsenic
Beryllium
Cadmium
Calcium
Chromium
Copper
Fluorine
Lead
Mercury
Manganese
Nickel
Selenium
Titanium
Uranium
Zinc

This list was selected to include species representing several categories of combustion behavior based on previous Radian studies and other published reports. These groups are as follows:

- elements with enrichment in fly ash (As, Cd, Cr, Cu, F, Hg, Ni, Pb, Se, Zn),
- elements with approximately equal distribution throughout the sized ash fraction (Ca), and
- elements with distributions in disagreement in the literature (Be, Mn, Ti).

In order to substanitiate the particle size of cyclone collected ash fractions, average particle size was determined by electron microscopy and specific surface area by BET adsorption analysis.

Composite samples of the coal required density separation to study association of element with the organic or inorganic phase of coal. The approach used in the sink-float study and the analytical techniques employed in sample characterization are described in this section. The analytical methods are described in detail in Appendix B.

4.1 Sink-Float Separation of Coal

To investigate the association of elements with the organic or inorganic phase of the coal, the composite coal samples from both stations were separated into different fractions by suspension in a liquid mixture of known specific gravity. The inorganic components of raw coal are denser than the organic fraction. The separating liquid is selected such that a lighter fraction will be supported (i.e., remain in suspension) while heavier components sink. In this study, mixtures of benzene and carbon tetrachloride were used as the separation liquors. Two separations were performed with mixtures with specific gravities of 1.35 and 1.45. This resulted in four density fractions which were subsequently analyzed and compared to the total coal composition.

The initial composite coal sample was dried, ground and reduced to <200 mesh. A 5 to 10 weight percent slurry of the coal and separation liquor was then prepared and allowed to settle. After 24 hours, the suspended coal was decanted from the container. Both sink and float fractions were retained for characterization. A schematic representing the separation is found in Figure 4-1.

4.2 Analytical Techniques

The techniques used for the quantitative determinations included:

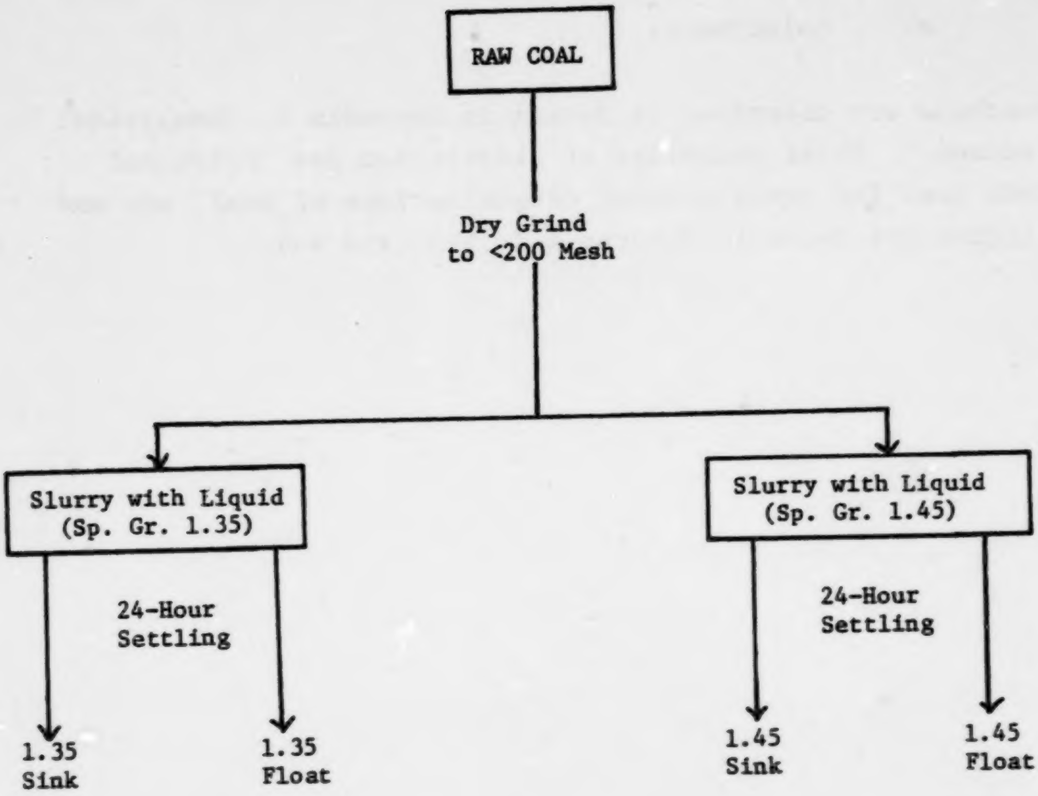
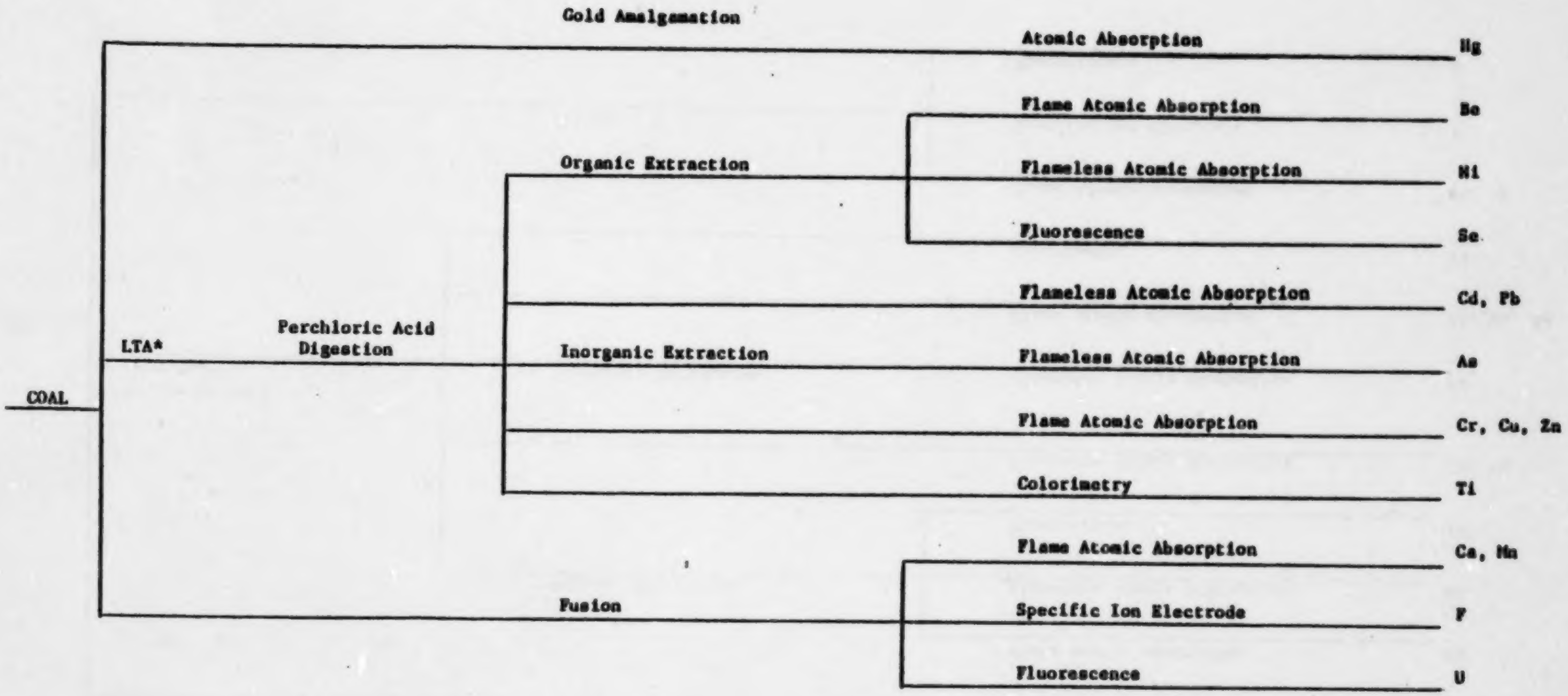

RAW COAL
Dry Grind
to <200 Mesh
Slurry with Liquid
(Sp. Gr. 1.35)
24-Hour
Settling
1.35
Sink
1.35
Float
Slurry with Liquid
(Sp. Gr. 1.45)
24-Hour
Settling
1.45
Sink
1.45
Float

Figure 4-1. Sink-Float Separation of Coal

- flame atomic absorption
- flameless atomic absorption,
- specific ion electrode,
- fluorometry, and
- colorimetry.

The methods are described in detail in Appendix B, "Analytical Procedures." Brief summaries of dissolution and analytical methods used for trace element determinations of coal, ash and WEP liquor are found in Figures 4-2, 4-3, and 4-4.


COAL
LTA*
Perchloric Acid Digestion
Gold Amalgamation
Organic Extraction
Inorganic Extraction
Fusion
Atomic Absorption
Flame Atomic Absorption
Flameless Atomic Absorption
Fluorescence
Flameless Atomic Absorption
Flameless Atomic Absorption
Flame Atomic Absorption
Colorimetry
Flame Atomic Absorption
Specific Ion Electrode
Fluorescence
Hg
Be
Ni
Se
Cd, Pb
As
Cr, Cu, Zn
Ti
Ca, Mn
F
U

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*LTA - Low Temperature Asher

Figure 4-2. Analytical Flow Chart for Coal Samples

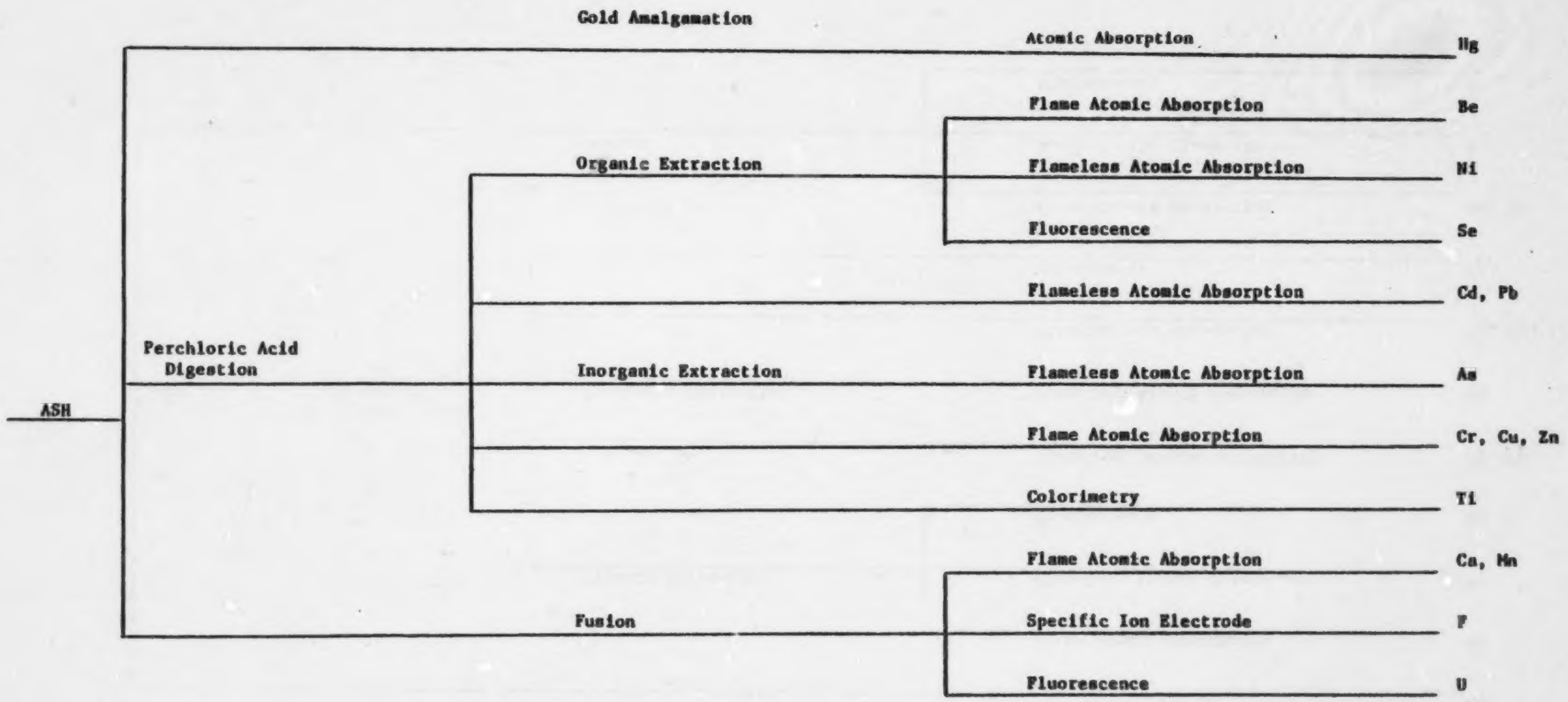

ASH
Perchloric Acid Digestion
Gold Amalgamation
Atomic Absorption
Hg
Organic Extraction
Flame Atomic Absorption
Be
Flameless Atomic Absorption
Ni
Fluorescence
Se
Flameless Atomic Absorption
Cd, Pb
Inorganic Extraction
Flameless Atomic Absorption
As
Flame Atomic Absorption
Cr, Cu, Zn
Colorimetry
Ti
Fusion
Flame Atomic Absorption
Ca, Mn
Specific Ion Electrode
F
Fluorescence
U

Figure 4-3. Analytical Flow Chart for Ash Samples

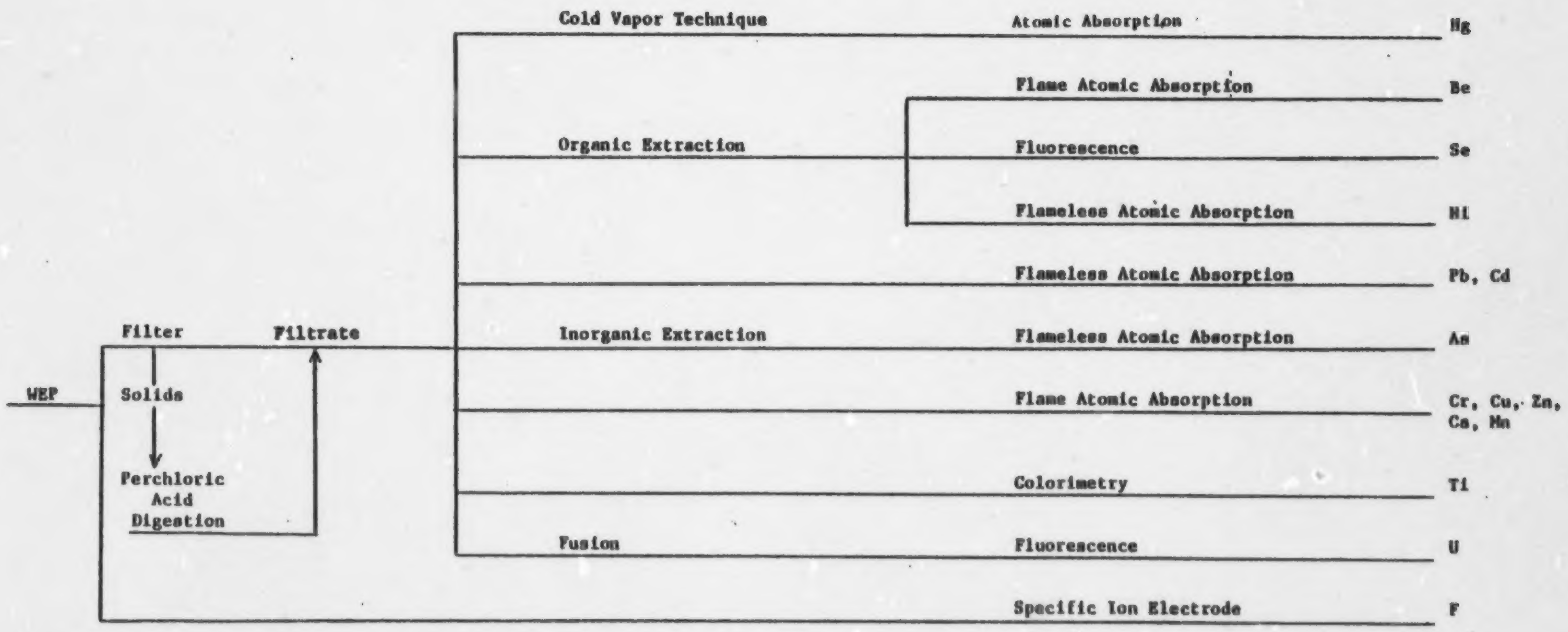

WEP
Filter
Solids
Perchloric Acid Digestion
Filtrate
Cold Vapor Technique
Organic Extraction
Inorganic Extraction
Fusion
Atomic Absorption
Flame Atomic Absorption
Fluorescence
Flameless Atomic Absorption
Flameless Atomic Absorption
Flameless Atomic Absorption
Flame Atomic Absorption
Colorimetry
Fluorescence
Specific Ion Electrode
Hg
Be
Se
Ni
Pb, Cd
As
Cr, Cu, Zn, Ca, Mn
Ti
U
F

Figure 4-4. Analytical Flow Chart for WEP Solution

5.0 RESULTS OF COAL CHARACTERIZATION STUDIES

This section presents the results of the coal analyses and the organic-inorganic elemental association study.

5.1 Chemical Analysis of Raw Coals

Proximate, ultimate and elemental analyses of composite coal samples from each station were performed. The results presented in Table 5-1 represent the average of duplicate determinations.

5.2 Sink-Float Separation Study of Coal

Coal fractions resulting from sink-float separation were analyzed to determine the concentration of 15 elements. The separation methodology was designed to separate each coal into four fractions as previously described in Section 4.1. The ash content (percent) and analytical results (ppm) for each coal fraction are presented in Table 5-2. The percentage of raw coal indicates the distribution of the coal sample between the sink and float fractions. The raw coal compositions are also tabulated here for comparison.

Coal HS was very uniform in specific gravity; 97% of the raw coal was within a specific gravity range of 1.35-1.45. Coal CS, on the other hand, was more diversified; only 45% of this coal exhibited density within that range.

Association of Elements with the Organic/Inorganic Phase of Coal

To correlate the analytical results for each station, the concentration of a given element in each sink-float fraction

TABLE 5-1. COAL ANALYSIS

	Coal HS		Coal CS	
	As Received	Dry	As Received	Dry
Proximate Analysis				
% Moisture	29.3	—	19.0	—
% Ash	5.4	7.7	9.2	11.4
% Volatile Matter	31.2	44.1	30.1	37.1
% Fixed Carbon	34.1	48.2	41.7	51.5
Btu/lb	7904	11181	9225	11388
% Sulfur	0.40	0.56	0.69	0.85
Ultimate Analysis				
% Moisture	29.3	—	19.0	—
% Carbon	47.4	67.0	54.6	67.4
% Hydrogen	3.2	4.5	3.6	4.4
% Nitrogen	0.7	1.0	1.0	1.2
% Chlorine	0.00	0.00	0.01	0.01
% Sulfur	0.40	0.56	0.69	0.85
% Ash	5.4	7.7	9.2	11.4
% Oxygen (Diff)	13.6	19.2	11.9	14.7
Elemental Analysis (ppm)				
Arsenic		1.2		3.9
Beryllium		1.05		0.85
Calcium		9380.0		3730.0
Cadmium		0.90		0.70
Chromium		14.0		13.0
Copper		14.0		14.0
Fluorine		52.0		54.0
Mercury		0.14		0.11
Manganese		24.0		34.0
Nickel		7.0		5.1
Lead		6.7		11.7
Selenium		1.2		1.8
Titanium		670.0		990.0
Uranium		0.90		2.0
Zinc		11.7		6.5

Values represent the average of duplicate determinations

TABLE 5-2. ANALYSIS OF COAL SINK-FLOAT FRACTIONS*

Coal Fraction	% of Raw Coal	% Ash**	As	Be	Ca	Cd	Cr	Cu	F	Hg	Mn	Ni	Pb	Se	Tl	U	Zn
Coal HS																	
Float at 1.35	1.6	5.8	1.5	1.00	8890	0.50	9.5	12	61	0.24	23	7.3	3.0	0.70	520	1.0	7.0
Float at 1.45	98.4	6.8	1.1	0.55	9280	0.47	19	12	60	0.12	24	5.0	4.1	1.1	620	0.88	5.8
Raw Coal	100	7.7	1.2	1.05	9390	0.90	14	14	52	0.14	24	7.0	6.7	1.2	670	0.90	11.7
Sink at 1.35	98.4	7.9	2.3	0.75	9240	1.4	11	17	67	0.14	23	5.9	5.4	1.4	660	0.83	7.5
Sink at 1.45	1.6	43.4	20	1.4	8460	8.6	31	70	190	2.0	41	18	43	6.1	2640	2.3	89
Coal CS																	
Float at 1.35	41.5	3.9	0.85	1.15	3100	0.55	16	6.3	25	0.11	27	4.4	5.9	1.6	450	1.4	4.0
Float at 1.45	86.5	5.6	1.2	1.60	3180	0.45	10	10	32	0.09	32	2.8	5.6	1.6	880	1.2	6.5
Raw Coal	100	11.4	3.9	0.85	3730	0.70	13	14	54	0.11	34	5.1	11.7	1.8	990	2.0	6.5
Sink at 1.35	58.5	18.4	9.3	0.95	4140	0.70	21	25	54	0.19	37	3.9	12.1	1.0	1110	1.5	8.9
Sink at 1.45	13.5	51.5	15.0	0.75	7975	1.2	14	43	92	0.40	50	5.1	16.0	4.5	2000	2.7	15.6

*All concentrations calculated on a dry weight basis and reported as ppm (µg/g) unless otherwise noted.

**Ash Content of the coal fraction.

All values represent the average of duplicate determinations.

was compared with the ash content of that fraction. Throughout this report, the ash component is considered to represent the mineral or inorganic portion of the coal. The ash-free component, on the other hand, is considered to be organic in nature. A linear least squares fit of ash content and concentration was performed for each element. Elemental concentrations were extrapolated to 0% and 100% ash values to estimate concentration of the element in each extreme case. In Figure 5-1 the concentration of copper is plotted versus ash content. Analogous figures for all 15 elements are included at the end of this section.

To establish the validity of assigning element concentrations to the 0% and 100% ash content fractions, estimated concentrations for each case were proportionally combined according to the ash content of the raw coal. The resulting concentration for most elements in the mathematically derived raw coal concentrations compares favorably with the analytical values for the raw coal. These results are presented in Table 5-3.

With an assigned element content in each extreme case, the association with organic or inorganic phase is identified by comparing the content of one phase to the calculated total content. The association of any element for the organic phase then can be represented as follows:

$$\text{\% Organic Association} = \frac{\text{Mass of Element in Organic Phase x 100}}{\text{Mass of Element in Total (Organic + Inorganic) Coal}}$$

$$= \frac{C_o \cdot (1-A)}{C_o \cdot (1-A) + C_{100} \cdot A} \times 100$$

where, C_o = extrapolated concentration of an element at 0% ash content,

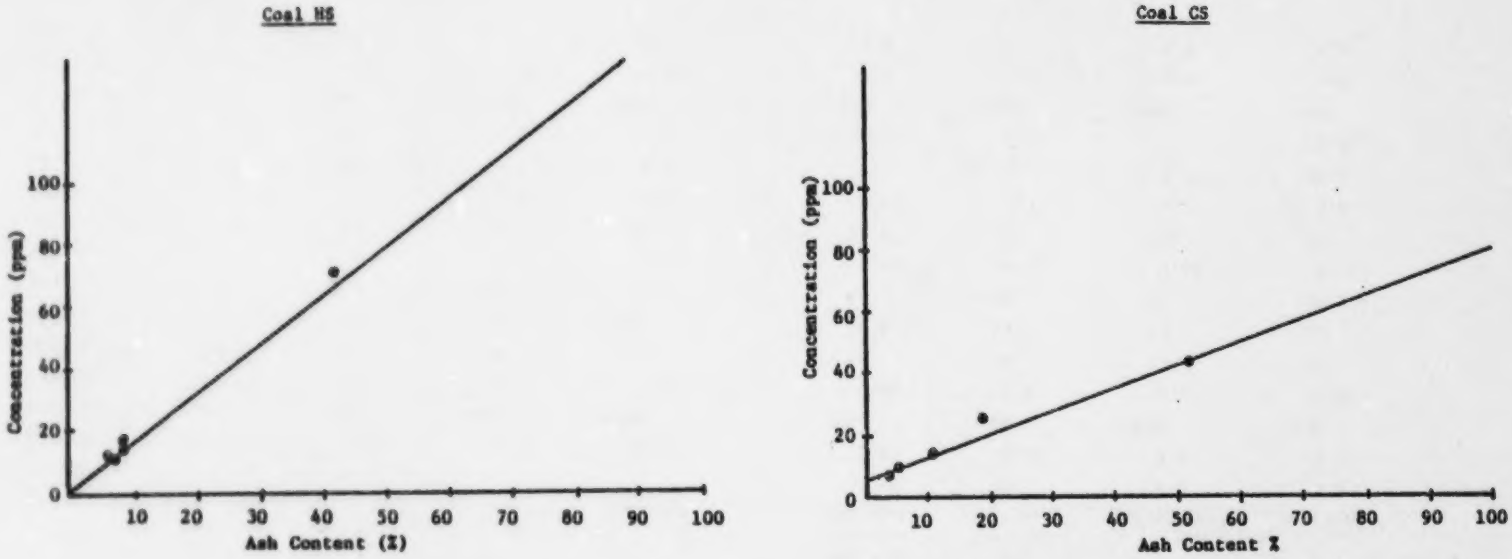


Figure 5-1. Copper Concentration vs Ash Content for Coal Fractions

TABLE 5-3. TRACE ELEMENT CONTENT OF THEORETICAL 0% AND 100% ASH FRACTIONS

	CONCENTRATION (ppm)							
	Coal HS (7.7% Ash)				Coal CS (11.4% Ash)			
	Ash-Free Fraction (0% Ash)	Ash Fraction (100% Ash)	Whole Coal		Ash-Free Fraction (0% Ash)	Ash Fraction (100% Ash)	Whole Coal	
Element			Calculated*	Analyzed			Calculated*	Analyzed
Arsenic	0	49	3.7	1.2	0.68	30	4.0	3.9
Beryllium	0.73	2.3	0.85	1.05	1.3	0.14	1.1	0.85
Calcium	9400	7350	9240	9390	2540	12900	3700	3730
Cadmium	0	21	1.6	0.90	0.46	1.9	0.62	0.70
Chromium	10	59	14	14	14	16	14	13
Copper	2.8	158	15	14	6.2	81	15	14
Fluorine	35	392	62	52	28	175	45	54
Mercury	0	4.8	0.4	0.14	0.061	0.72	0.14	0.11
Manganese	20	68	24	24	28	72	33	34
Nickel	4.1	36	6.6	7.0	3.8	6.3	4.1	5.1
Lead	0	103	8	6.7	6.6	27	8.9	11.7
Selenium	0.12	14	1.2	1.2	0.96	7.2	1.7	1.8
Titanium	225	5800	650	670	580	3400	900	990
Uranium	0.64	4.4	0.93	0.90	1.3	4.0	1.6	2.0
Zinc	0	215	17	11.7	4.2	27	6.8	6.5

---

*Mathematically calculated concentration derived by combining 0% and 100% ash fractions in the ratio found in raw coal.

C_{100} = extrapolated concentration of an element at 100% ash content, and

A = fraction of ash in raw coal sample.

The coal phase association results of this study are presented in Table 5-4. All elements are ranked numerically according to their calculated association with the organic (ash-free) portion of the coal. Comparison is made with the results reported by Gluskoter (GL-077) for another western coal, Black Mesa coal from Arizona. Table 5-5 includes the results of Gluskoter (GL-077) for four eastern coals. The four categories indicated in the table are defined on the basis of the fraction of an element found in the organic phase. The ranges of elemental fractions generally used for each category are as follows:

- organic - >0.66,
- intermediate organic - 0.50-0.66,
- intermediate inorganic - 0.33-0.49, and
- inorganic - <0.33.

From Tables 5-4 and 5-5 the following specific observations can be made regarding the three western coals:

- calcium displays an extremely high organic association in Coal HS, while in the other two only intermediate organic association is noted (in most eastern coals Ca is found with the mineral phase);

- beryllium and nickel are consistently associated with the organic phase in all three western coals;

TABLE 5-4. COMPARISON OF ORGANIC ASSOCIATION OF WESTERN COALS

	Coal HS Wyoming	Coal CS Wyoming	Black Mesa Coal ** Arizona
Calcium	94*	60	66
Nickel	89	82	89
Beryllium	82	98	81
Manganese	78	78	51
Chromium	67	87	54
Uranium	63	71	53
Fluorine	52	58	NR
Titanium	32	73	31
Copper	18	37	74
Selenium	10	56	60
Cadmium	0	65	NR
Lead	0	66	7
Arsenic	0	15	9
Zinc	0	55	NR
Mercury	0	40	20

---

*Organic association as %

**Source GL-077

NR - Not reported

TABLE 5-5. RANKING OF ELEMENTS IN COAL ACCORDING TO ORGANIC-INORGANIC AFFINITIES

	Coal HS Wyoming	Coal CS Wyoming	Black Mesa Coal Arizona*	Clochester Coal Illinois*	Davis Coal Illinois*	Blue Creek Coal Alabama*	Pittsburgh #8 Coal West Virginia*
Organic	Ga Ni Be Mn Cr	Be Cr Ni Mn Ti U	B Na P Mg Ba Fe S Ni Co Br Sr Ca Be Dy Yb Cu V Lu Sb	Ge P Be B Ga	Ge B Be P Se Sb Cr	Br Ge Co S Ni V Cu Dy Sr Be V La U	Sr Br B U Na P S Dy Ge
Intermediate Organic	U F	Pb Cd Ca F Se Zn	Sc Ce Sm La Eu Cr Tb U Mn W	Sb Co Se Na V K Ni	Co Ga Ca Ni K V	Pb Sm Tb Eu Sb Ce Ba Ga P	Pb Eu Na Be Co Ga Ca V
Intermediate Inorganic	Ti	Hg Cu	K Sm Hf Zr Ta Al Th Ga	Pb Cu Si Al Zr S Hg	Al Cu Si Mn	Cr Zr Se Yb Ti Sc Lu Fe Hf Th Al	Cu Hg La Sm Ni Zn Sb Sn Mn Cr Ce Sc Se Tb
Inorganic	Cu Se Cd Pb As Zn Hg	As	Rb Ti Sn Hg As Si Pb Co Ge	Fe As Mo Cd Cr Mn Zn Co	Zr S As Cd Hg Mo Pb Zn Fe	Ta B Ca Zn Na Si K Mg Ce Rb Mn As	Yb Al Fe Hf Lu Zr As Ta Th Rb K Si Ca Ti

*Source: GL-077

- chromium, manganese and uranium exhibit higher organic association in the two Wyoming coals than in the Arizona coal; manganese is primarily inorganically bound in eastern samples, while chromium is not consistent in phase association;

- fluorine is not primarily associated with either phase,

- titanium is organically associated in the coal CS, while inorganic association is prevalent in the other two western coals;

- copper in the Wyoming coals is found associated with the mineral matter while organically combined in the Arizona coal;

- selenium, cadmium, lead, zinc and mercury are completely inorganically associated in Coal HS, no extreme preferential association is apparent in Coal CS;

- arsenic is primarily associated with the inorganic phase in both eastern and western coals,

- while Coal CS has a higher ash content, there is a lower degree of association of the elements analyzed with the ash or mineral phase. On the other hand, five elements (Cd, Pb, As, Zn, Hg) exhibit 100% association with the mineral phase in the Coal HS even though this coal has a lower ash content than Coal CS.

The following figures present plots of element concentration versus ash content derived in the sink-float coal separation and analysis study.

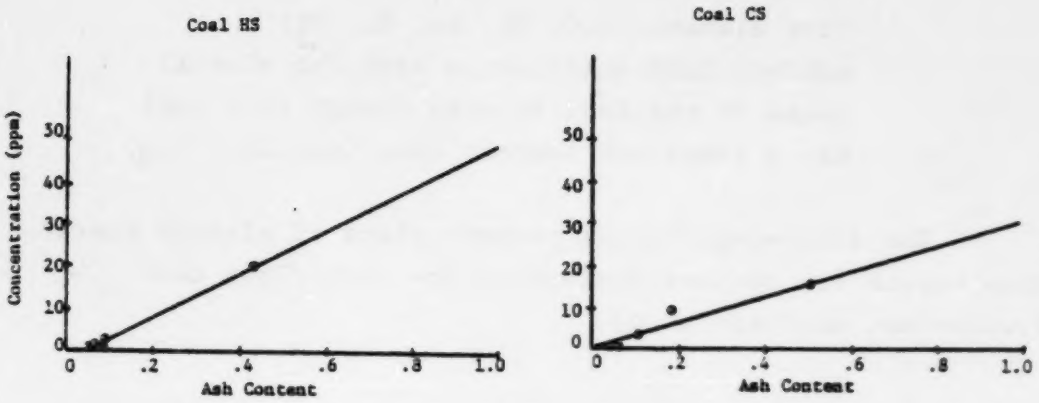


Figure 5-2. Arsenic Concentration vs Ash Content

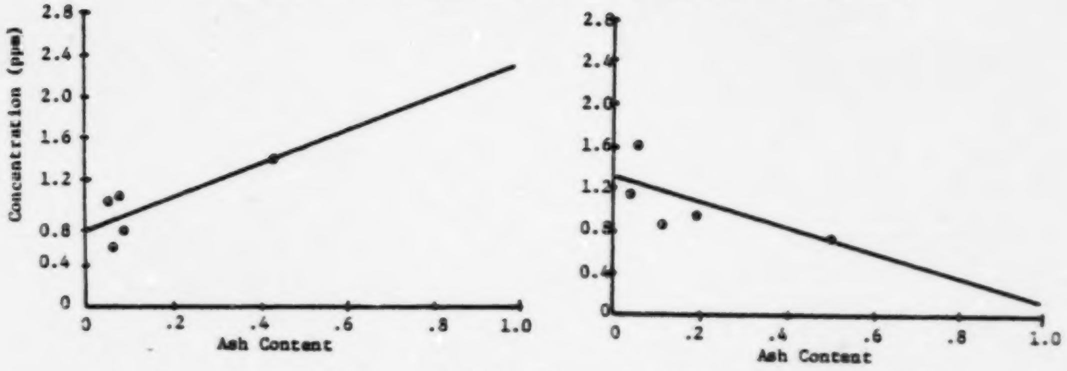


Figure 5-3. Beryllium Concentration vs Ash Content

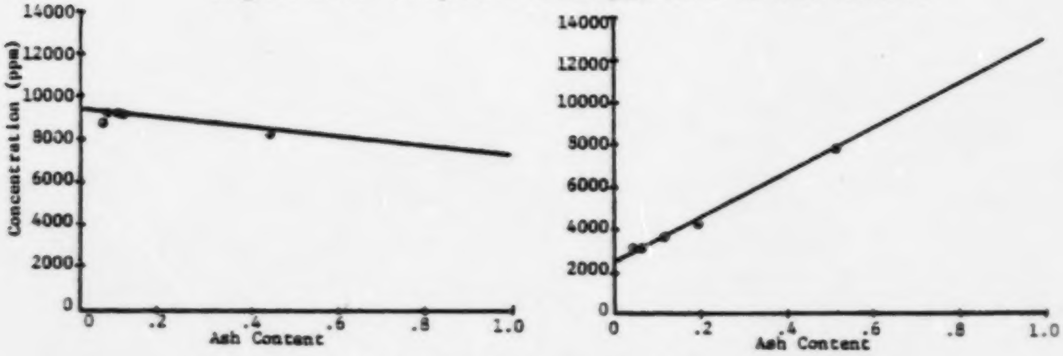


Figure 5-4. Calcium Concentration vs Ash Content

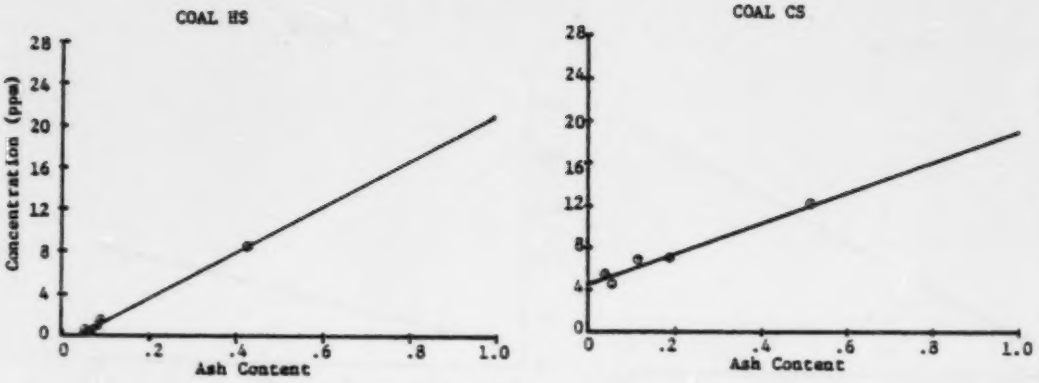


Figure 5-5. Cadmium Concentration vs Ash Content

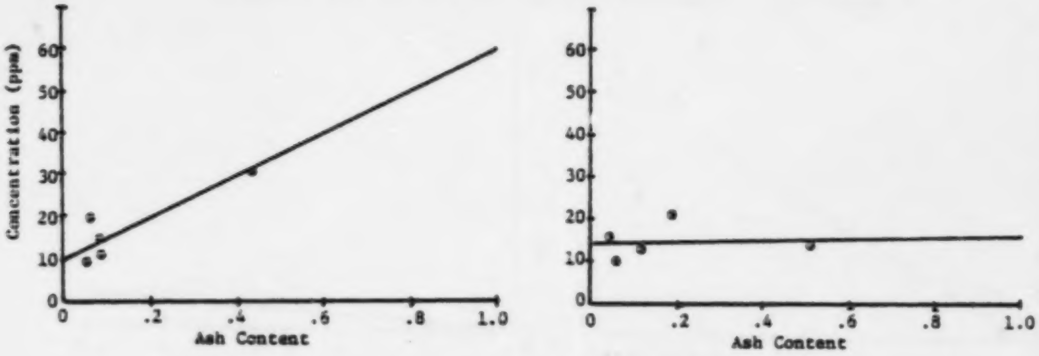


Figure 5-6. Chromium Concentration vs Ash Content

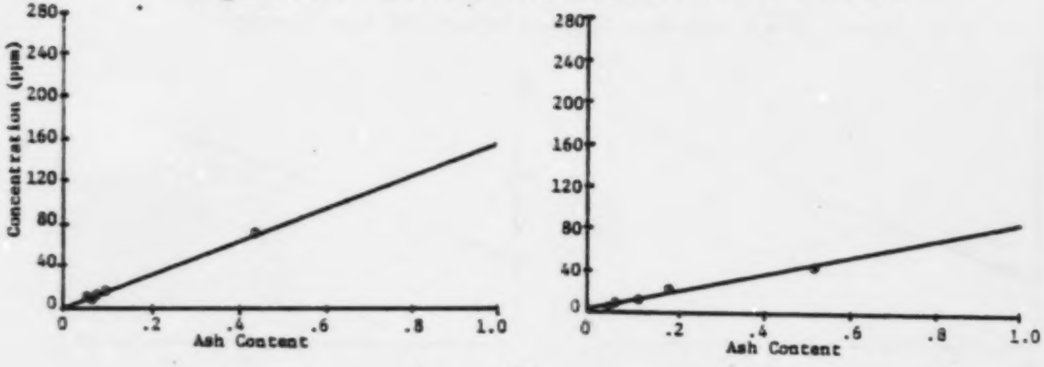


Figure 5-7. Copper Concentration vs Ash Content

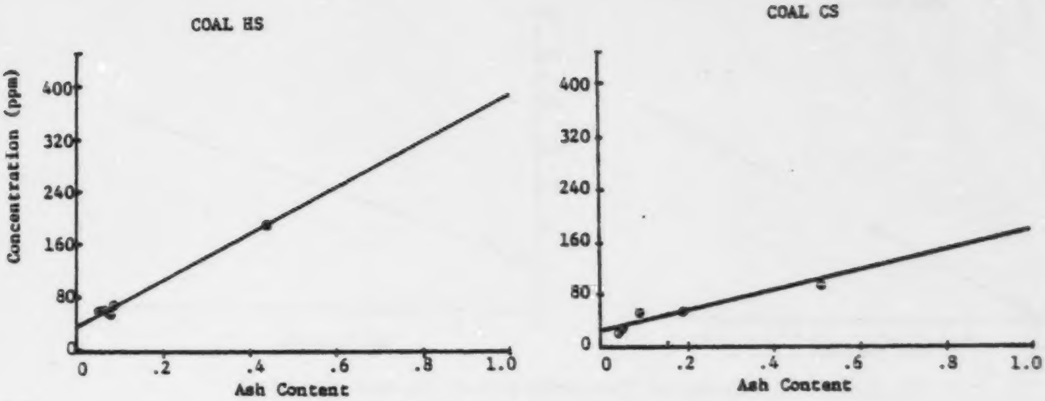


Figure 5-8. Fluorine Concentration vs Ash Content

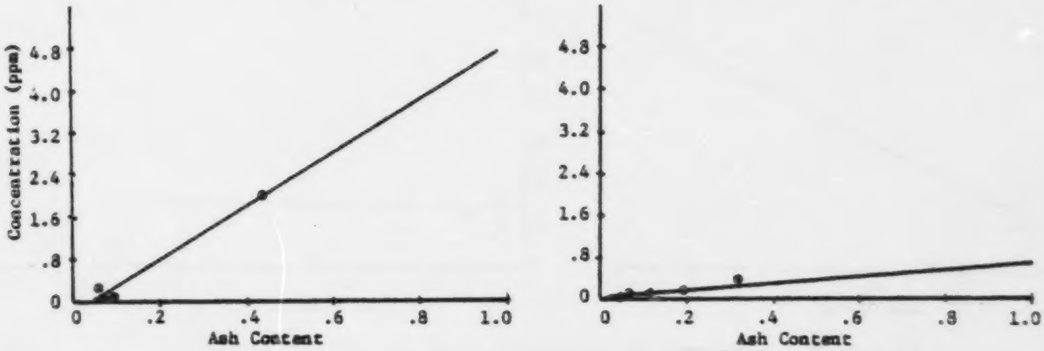


Figure 5-9. Mercury Concentration vs Ash Content

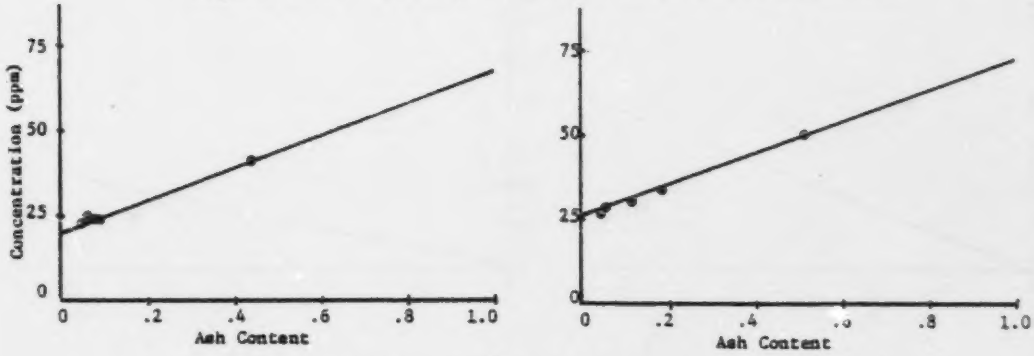


Figure 5-10. Manganese Concentration vs Ash Content

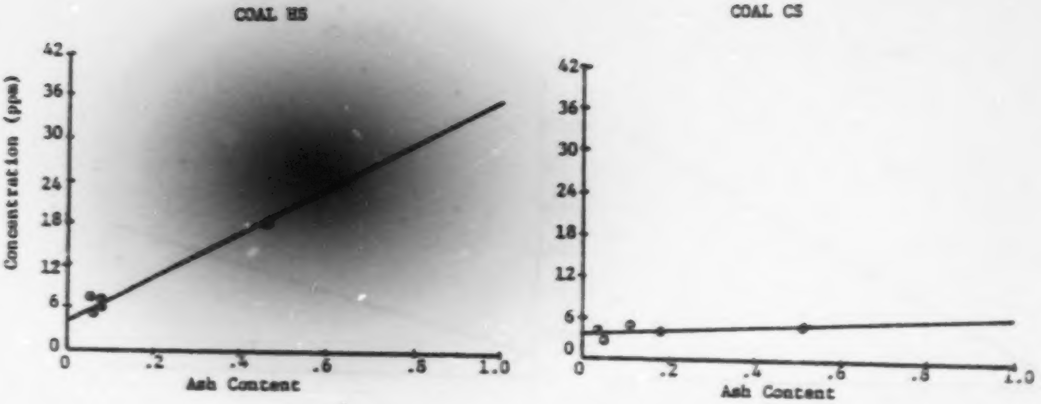


Figure 5-11. Nickel Concentration vs Ash Content

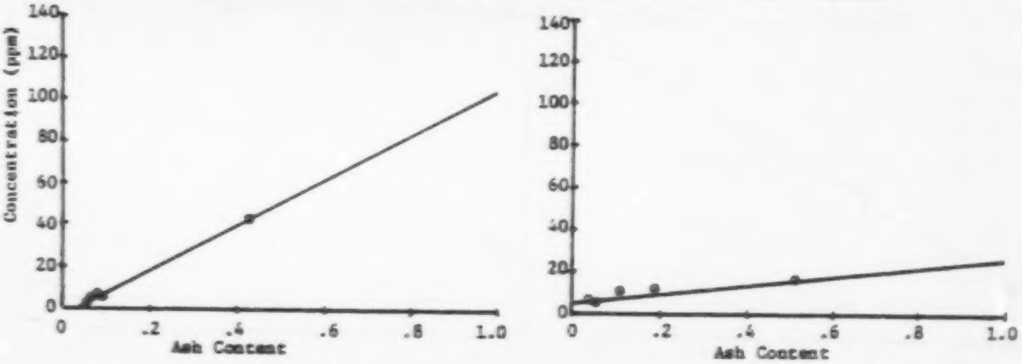


Figure 5-12. Lead Concentration vs Ash Content

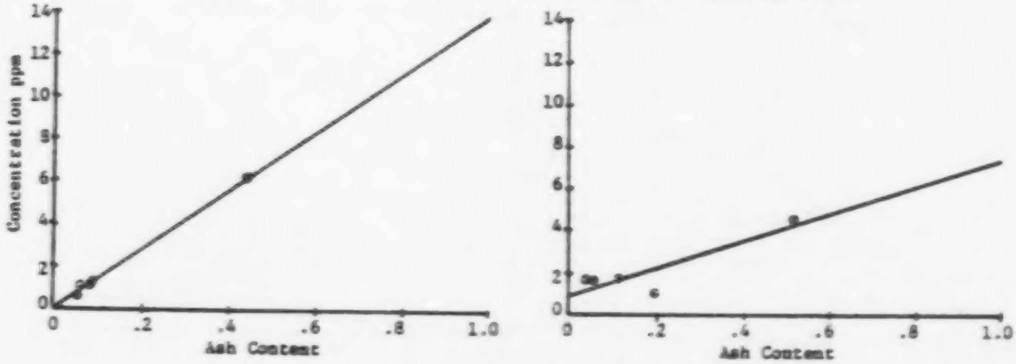


Figure 5-13. Selenium Concentration vs Ash Content

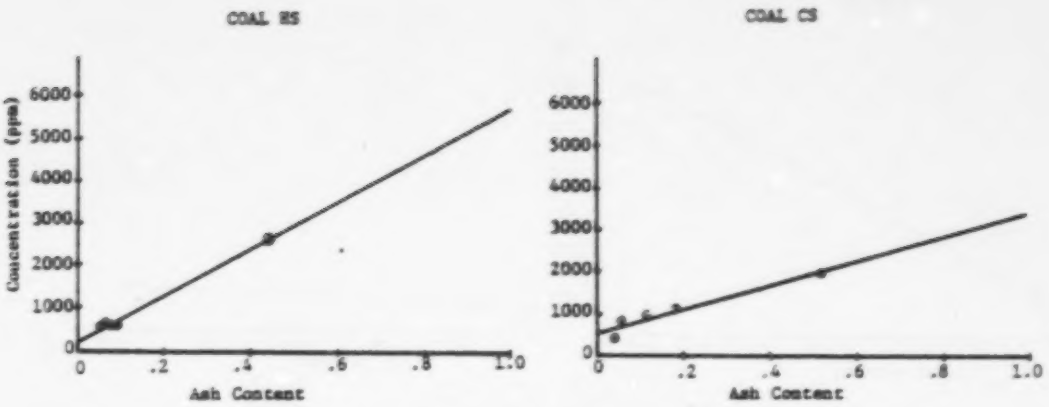


Figure 5-14. Titanium Concentration vs Ash Content

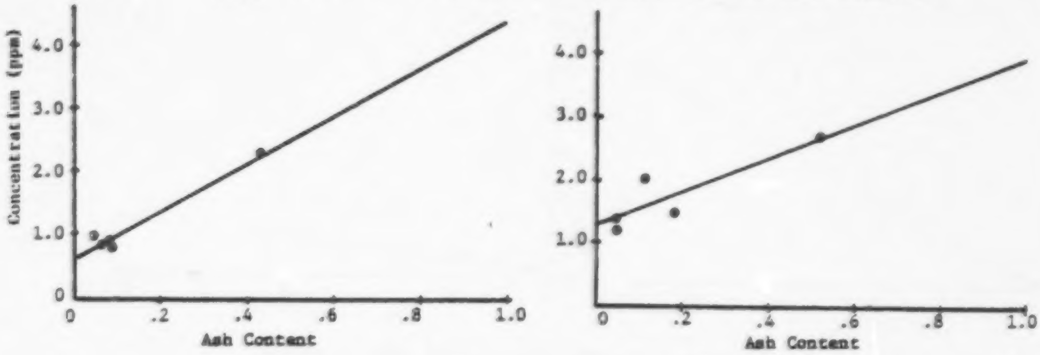


Figure 5-15. Uranium Concentration vs Ash Content

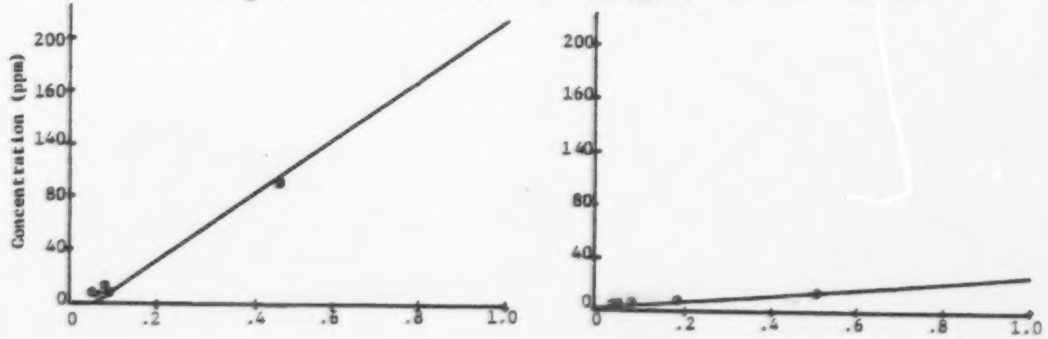


Figure 5-16. Zinc Concentration vs Ash Content

6.0 RESULTS OF ELEMENT ENRICHMENT STUDY

This section presents and discusses the results of the fly ash element enrichment study. This part of the program involved physical and chemical characterizations of selected particulate samples. Data analysis involved application of mathematical techniques to calculate enrichment in each sized fraction and the composite ash-vapor samples. In this program, enrichment of an element was defined so as to be independent of other chemical species present. This approach differs from that used in other studies in that other definitions assumed even distribution of some selected species (e.g., Ca, Al or Fe) throughout all ash fractions. This has not been shown to be consistently true in every case, according to previous Radian work and other literature.

The results of this study are presented in the following order:

- physical characterization of cyclone sized ash,
- element concentration and enrichment ratios for cyclone ash,
- element concentration and enrichment ratios for Andersen samples, and
- discussion of results.

6.1 Physical Characterization of Cyclone Collected Ash

The sized fly ash fractions collected by the cyclones in the HVSASS train were physically characterized with respect to particle size and surface area. Table 6-1 presents the results of these measurements.

TABLE 6-1. PHYSICAL CHARACTERISTICS OF CYCLONE PARTICULATES

	Particle Size Range, μ		Mean	Specific Surface Area, m^2/g	
	Expected[1]	Observed[2]	Diameter[2], μ	Calculated[3]	BET
Station HS:					
Cyclone 1	>14	4.8-0.4	2.0	1.2	1.9
Cyclone 2	14-4	3.8-0.4	1.9	1.2	1.9
Cyclone 3	4-1	1.8-0.3	0.8	3.0	4.0
Station CS:					
Cyclone 1	>14	8.7-0.5	2.0	1.2	IS
Cyclone 2	14-4	4.4-0.3	1.8	1.3	2.3
Cyclone 3	4-1	2.1-0.4	0.9	2.9	3.5

---

[1] Cyclone system designed for these size ranges.

[2] Mean diameter and range determined by count of SEM photographs of the ash.

[3] Surface area calculated assuming spherical particles, density of 2.5 g/cm^3 and observed mean diameters.

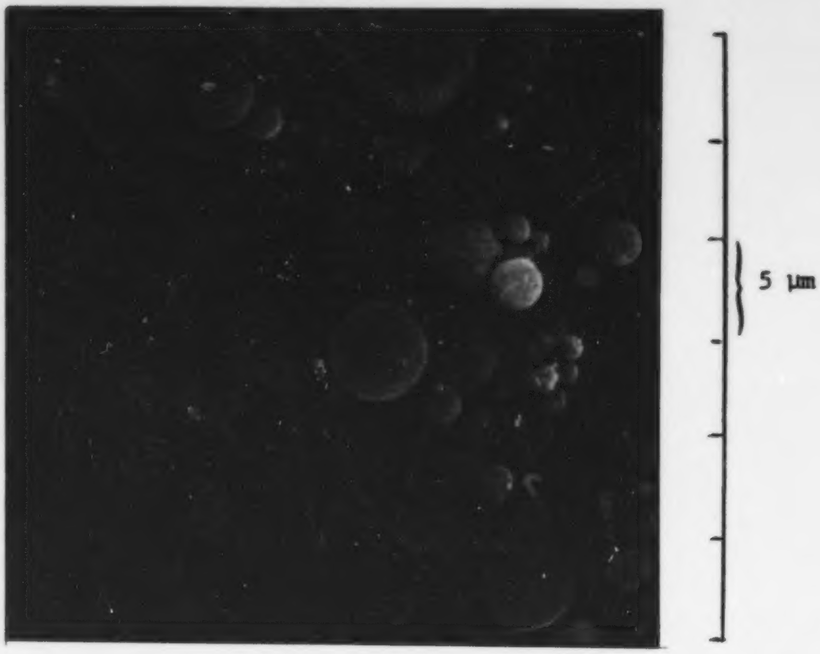
IS - insufficient sample for analysis.

The expected collection ranges were defined by cyclone cut-off diameters for the High-Volume Source Assessment Sampling System. The mean particle diameter and observed range were determined by numerical particle size counts of photomicrographs obtained by scanning electron microscopy (SEM).

A four-point BET surface area analysis was performed for each ash fraction. Calculated surface area was estimated based on the mean particle diameter, observed spherical shape and an assumed fly ash density of 2.5 g/cm^3 (KA-192). Density determination of precipitator ash at each station were performed ($\rho_{HS} = 2.6$, $\rho_{CS} = 2.5$) to validate the assumed density since insufficient quantities of fly ash were available for analysis.

The calculated surface areas were lower than measured values for all analyzed ash fractions. Visual inspection of the fly ash as shown by the SEM photomicrographs (Figures 6-1 through 6-6) indicates that the particles, though spherical in shape, have rough irregular surfaces. This irregular surface, although not considered in calculating the estimated area, actually increases the overall surface area. This is thought to be the reason for the difference between observed and calculated values, and substantiates the BET surface area results.

The particle size characteristics of the flue gas particulates from the two plants were quite similar. The SEM photomicrographs reveal the absence of large fly ash particles (>30μ) in the exiting flue gas. Although designed to collect >14μ particles, the first cyclone contained a significant amount of fine ash. In fact, the lower limits of the particle size ranges for all six cyclone samples (three each from both plants) are nearly identical. The presence of fines coupled with the absence of large particles resulted in the observed mean diameter for all collected fractions being below the expected particle size range for each fraction.



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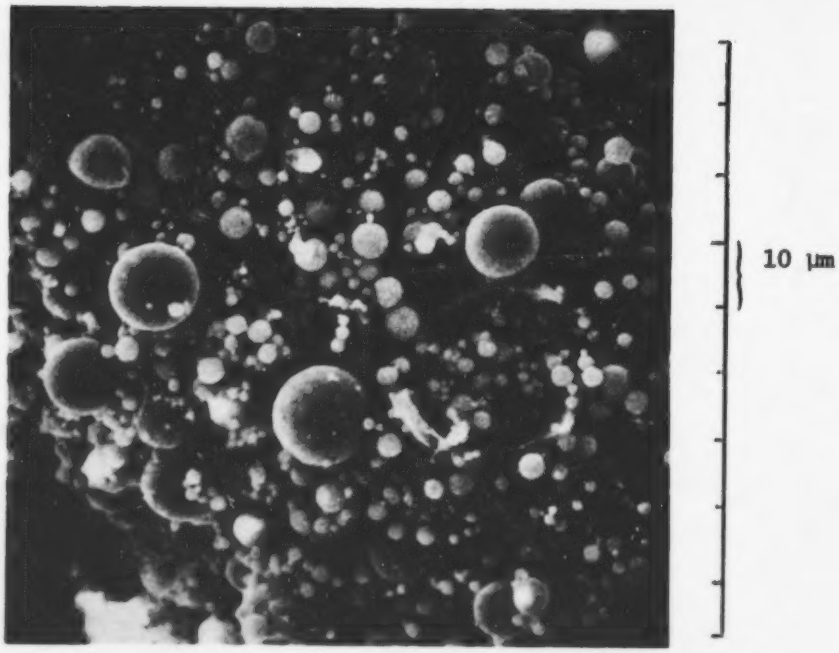

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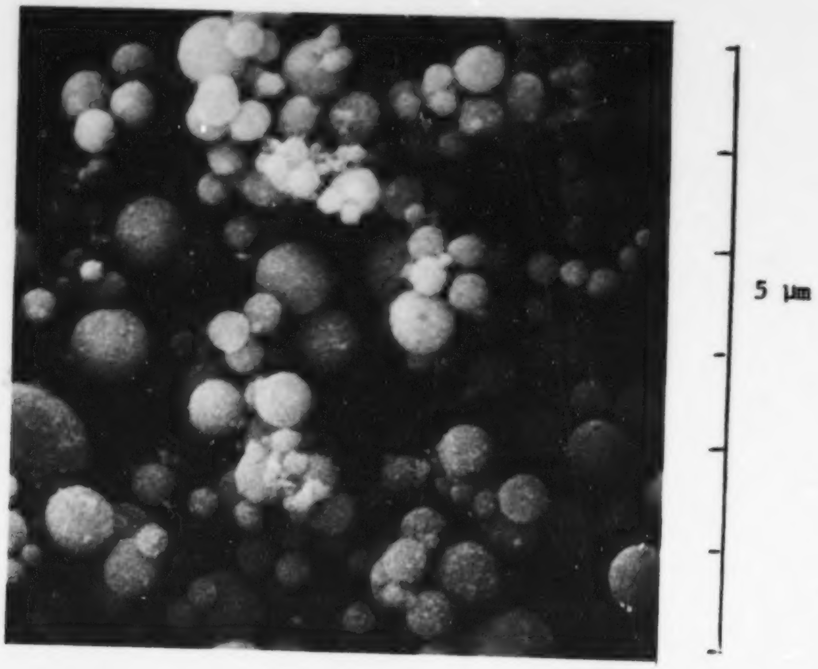
Figure 6-1. Cyclone #1 - Fly Ash Collected at Station HS.



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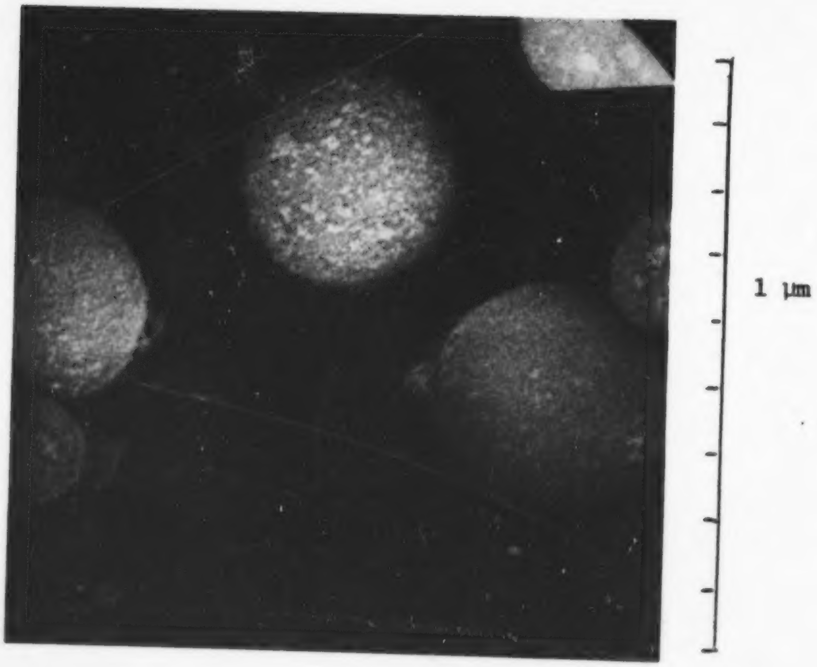

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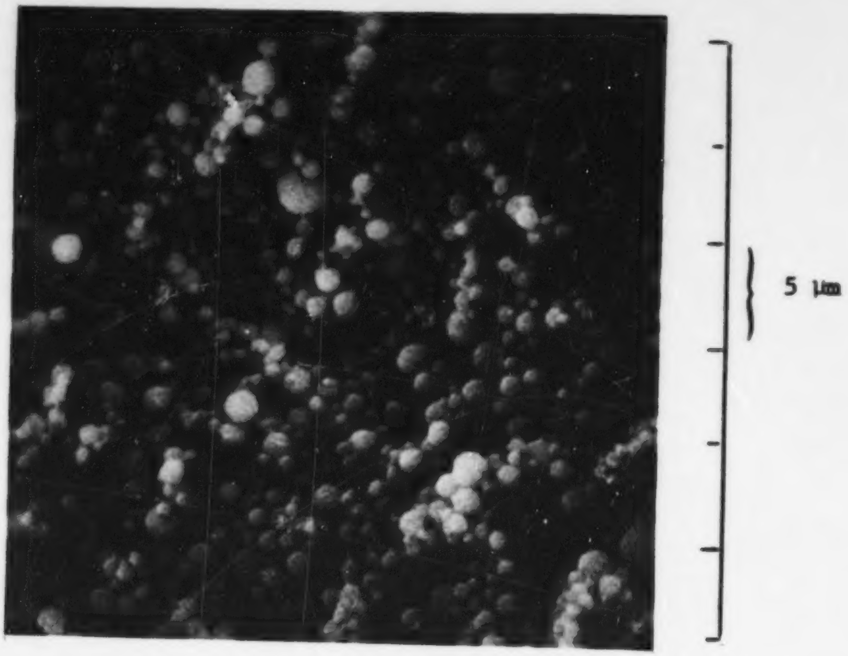
Figure 6-2. Cyclone #2 - Fly Ash Collected at Station HS.



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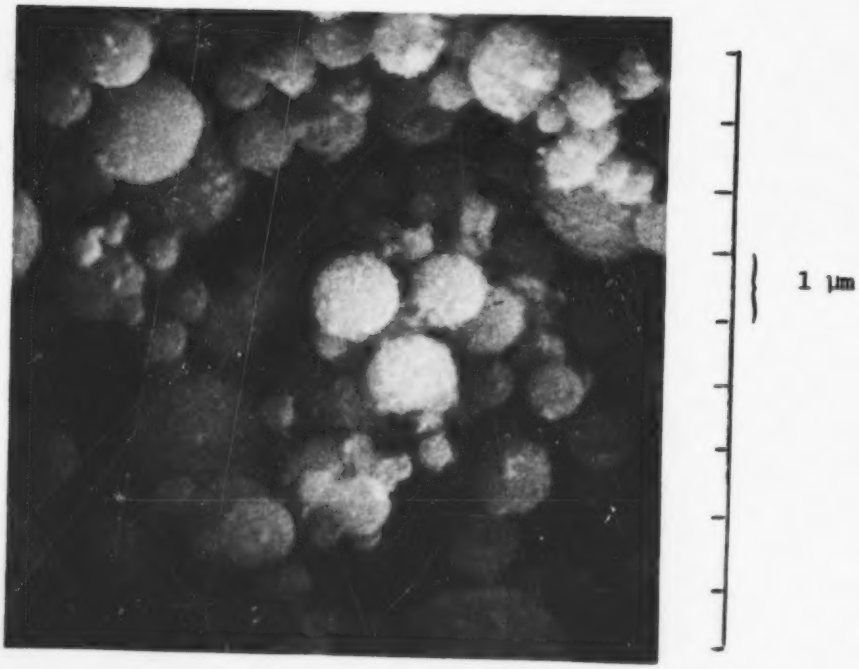

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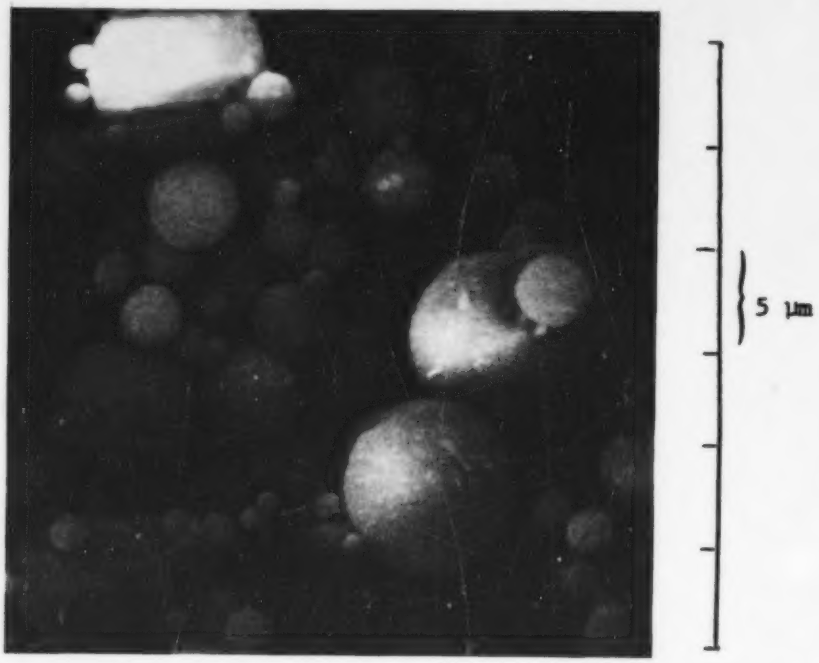
Figure 6-3. Cyclone #3 - Fly Ash Collected at Station HS.



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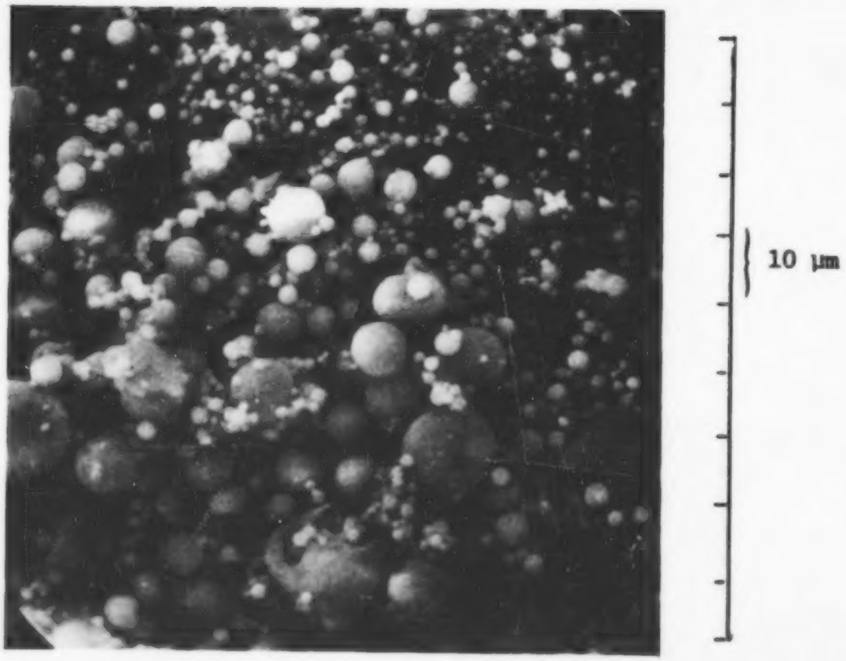

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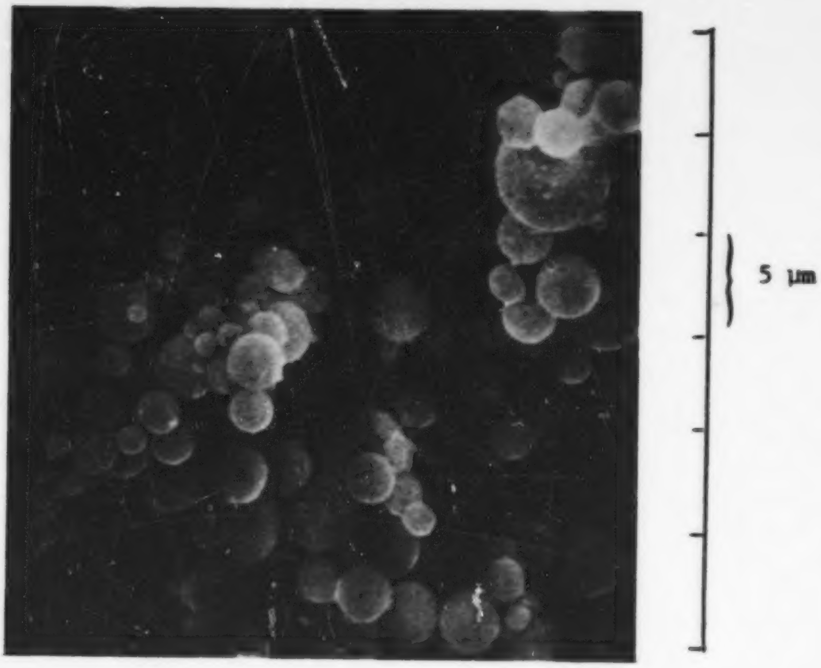
Figure 6-4. Cyclone #1 - Fly Ash Collected Station CS.



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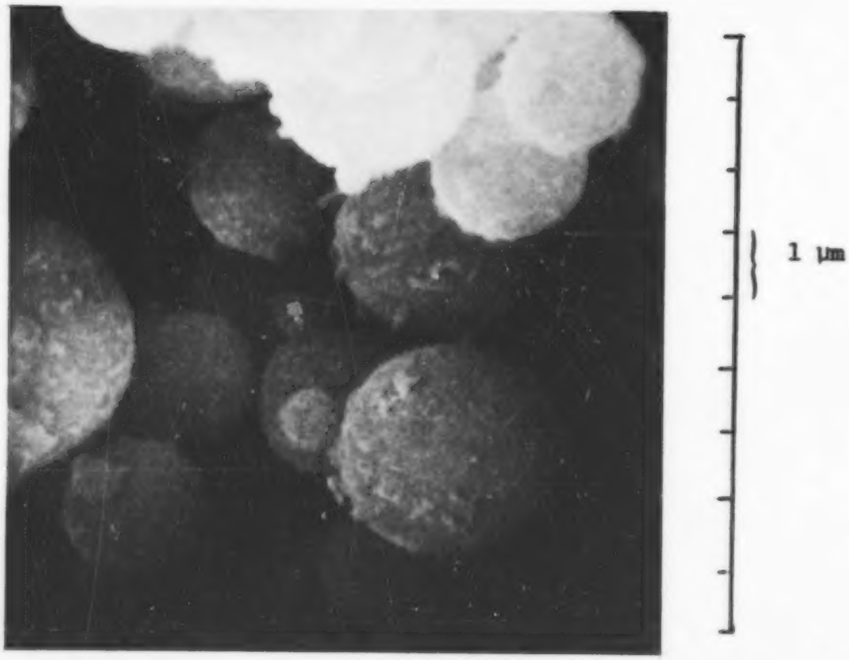

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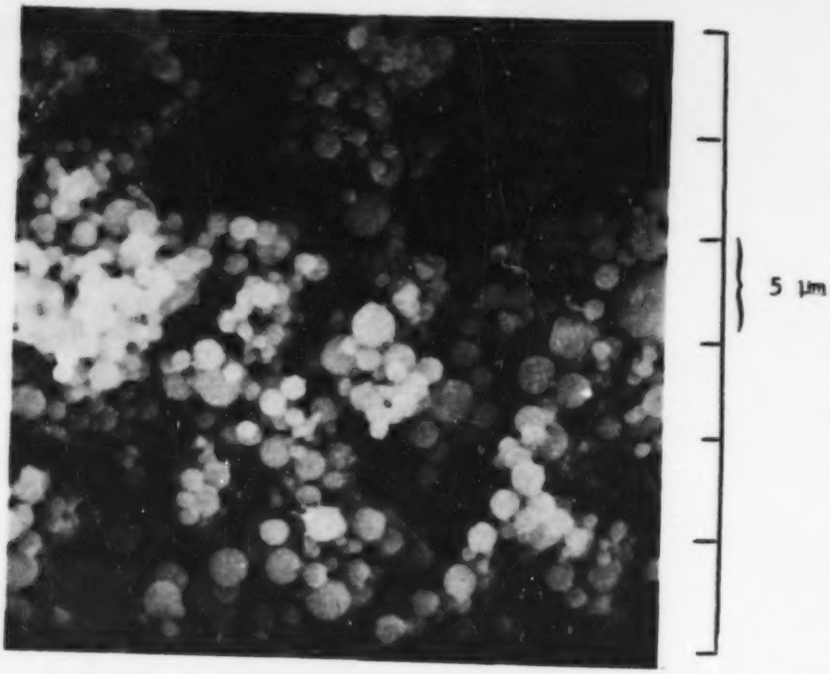
Figure 6-5. Cyclone #2 - Fly Ash Collected at Station CS.



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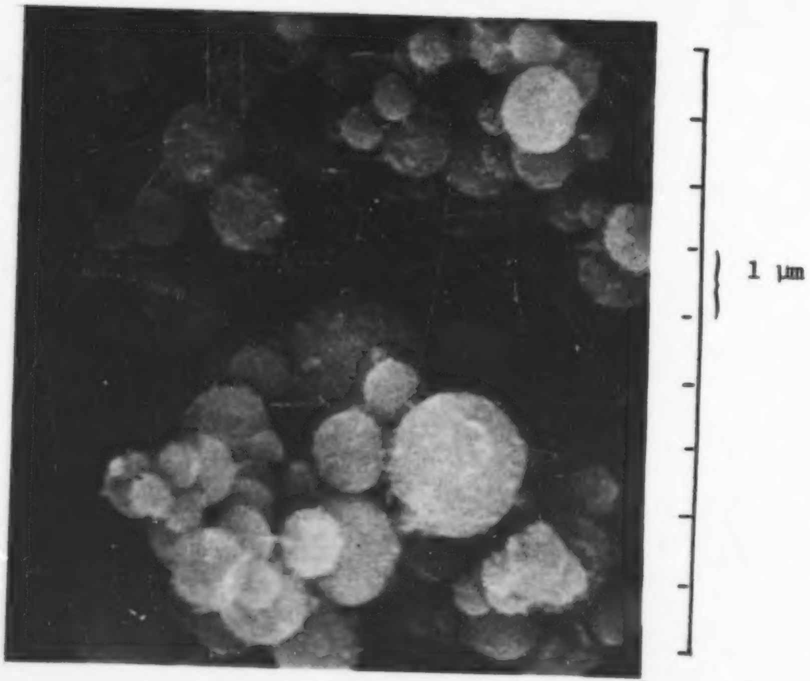

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Figure 6-6. Cyclone #3 - Fly Ash Collected at Station CS.

In addition, the average particle size of the first and second cyclone fractions were found to be very similar. This can be seen in Figures 6-1 and 6-2 of Station HS ash and Figures 6-4 and 6-5 of Station CS ash. Considering the similarity of the ash collected in these two cyclones these fractions were combined as a single sample for chemical analysis and subsequent enrichment studies.

One possible explanation for the discrepancies between expected and observed particle size in the cyclone fractions is agglomeration. Clusters of ash particles were identified in the photomicrographs. Agglomeration may take place either in the precipitator or in the exiting gas. In the ESP, charged particles are impacted on the plates, resulting in particulate build-up. Build-up is reduced by rapping of plates to allow gravity settling. Lighter particle clusters are susceptible to transport by the exiting flue gas. Also, clustering can result from impaction of charged gas particles in the cyclone collector. Particle clustering could result in effectively larger particle diameters (as seen by the cyclone fractionators) than were determined by SEM photomicrographic techniques, thus resulting in a greater degree of impaction earlier in the cyclone sampling train.

6.2 Element Concentration and Enrichment Ratios of Cyclone Collected Fly Ash

Results of elemental analyses of cyclone collected ash fractions are presented on a dry weight basis in Table 6-2. Also included is the average concentration of the fly ash (including vaporous species collected by the WEP) and the ash equivalent concentration of the raw coal for comparison. The average fly ash concentration is the result of proportionally combining the ash fraction concentrations according to the collection distribution

TABLE 6-2. ANALYTICAL RESULTS OF CYCLONE COLLECTED FLY ASH FRACTIONS.

Fly Ash Fraction	Concentrations as ppm Dry Weight Basis Unless Indicated Otherwise															Ash Fraction Distribution
	As	Be	Ca (%)	Cd	Cr	Cu	F	Hg	Mn	Ni	Pb	Se	Ti	U	Zn	
Station HS:																
Cyclones 1 & 2 (2.0μ)	58	3.0	16.5	5.0	150	235	860	0.24	190	101	73	59	8190	9.6	122	66.1%
Cyclone 3 (0.8μ)	62	2.4	16.8	9.3	110	360	1010	0.11	240	104	220	82	7830	9.7	225	28.7%
WEP (<0.8μ + Vaporous)	70	48	--	77	710	720	6.6%	190	240	580	--	710	(8000)*	19.5	650	5.2% 100.0%
Average Fly** Ash	60	5.1	—	9.9	167	295	4250	9.9	207	126	--	99	8080		179	
Ash Equivalence of Coal	15.6	13.6	12.2	11.7	182	182	675	1.8	312	91	87	15.6	8700	11.7	152	
Station CS:																
Cyclones 1 & 2 (1.9μ)	86	5.9	5.1	8.7	270	235	670	0.11	624	130	155	21	7950	21	250	41.1%
Cyclone 3 (0.9μ)	103	5.1	4.4	3.4	230	400	1120	0.14	980	120	330	29	8870	22	305	41.8%
WEP (<0.9μ + Vaporous)	102	64	--	64	865	1.8%	35.5%	476	675	650	--	187	(8400)*	41	2.27%	17.1% 100.0%
Average Fly** Ash	96	16	--	16	355	3340		82	780	215	—	53	8400	24	4100	
Ash Equivalence of Coal	34	7.4	3.3	6.1	114	123	474	0.96	298	45	103	15.8	8680	17.5	57	

All values represent the average of duplicate determinations.

*Titanium values are average of cyclone collected fly ash. Calcium and lead content of WEP was not determined due to precipitation as the sulfate by WEP electrolyte solution.

**Calculated by combining the individual ash concentrations in proportion to the ash distribution by HVSASS cyclone collection.

in the cyclone/WEP sampling train. The ash equivalent concentration is defined as that concentration of the element in the ash if all of the element originally in the coal were retained with the mineral content after combustion:

$$C_{cae} = \frac{C_c}{X_a} \qquad (6\text{-}1)$$

where,

C_{cae} = ash equivalent concentration of coal
C_c = element concentration of raw coal
X_a = ash content of coal.

For example, the hot-side coal with 1.20 ppm As and 7.7% ash has an ash equivalent concentration of:

$$C_{cae}(\text{As}) = \frac{1.20 \text{ ppm}}{.077} = 15.6 \text{ ppm As}$$

Enrichment Ratios

Enrichment ratios is defined as the ratio of an element's concentration in a given ash fraction to its ash equivalent concentration in the coal.

$$ER_x = \frac{Ca_x}{C_{cae_x}} \qquad (6\text{-}2)$$

where,

ER_x = enrichment ratio for element x
Ca_x = concentration of element x in the ash fraction
C_{cae_x} = ash equivalent concentration of element x in the coal.

Ratios greater than 1.0 indicate enrichment of the ash while those less than 1.0 indicate depletion of an element.

As mentioned previously, the use of this enrichment definition provides a means to quantify enrichment for an element independently of other chemical species present. Enrichment ratios for three cyclone-sized fractions are presented in Table 6-3. Those elements found enriched in all fractions, i.e., ratios greater than 1, include:

Station HS

Arsenic
Copper
Fluorine
Nickel
Selenium

Station CS

Arsenic
Chromium
Copper
Fluorine
Manganese
Nickel
Selenium
Uranium
Zinc

Those elements, although not enriched in all fractions but displaying increasing enrichment in the smaller fractions, include:

Station HS

Beryllium
Cadmium
Chromium
Mercury
Uranium
Zinc

Station CS

Beryllium
Mercury

TABLE 6-3. ENRICHMENT RATIO* FOR CYCLONE COLLECTED FLY ASH FRACTIONS

	Station HS				Station CS			
Element	2.0μ	0.8μ	<0.8μ	Σ**	2.9μ	0.9μ	<0.9μ	Σ**
As	3.7	4.0	4.5	3.8	2.5	3.0	3.0	2.8
Be	0.22	0.18	3.5	0.38	0.80	0.69	8.6	2.1
Ca	1.35	1.38	ND	ND	1.56	1.34	ND	ND
Cd	0.43	0.79	6.6	0.85	1.4	0.56	10	2.6
Cr	0.82	0.60	3.9	0.92	2.4	2.0	7.6	3.1
Cu	1.3	2.0	4.0	1.6	1.9	3.2	146	27
F	1.3	1.5	98	6.3	1.4	2.4	750	130
Hg	0.13	0.06	106	5.5	0.11	0.15	495	84
Mn	0.61	0.77	0.77	0.66	2.1	3.3	2.3	2.6
Ni	1.1	1.1	6.4	1.4	2.9	2.7	14	4.7
Pb	.84	2,5	ND	ND	1,5	3,2	ND	ND
Se	3.8	5.2	46	6.3	1.3	1.8	12	3.3
Ti	0.94	0.90	0.92	0.93	0.92	1.0	0.97	1.0
U	0.82	0.83	1.7	0.87	1.2	1.3	2.3	1.4
Zn	0.80	1.5	4.3	1.2	4.4	5.4	400	72
Ash Fraction Distribution	66.1%	28.7%	5.2%	100%	41.1%	41.8%	17.1%	100%

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*Ratio of ash fraction concentration to ash equivalent concentration of coal.

**Mean enrichment of flue gas particulate fractions determined by combining the individual values in proportion to the ash distribution by HVSASS cyclone collection.

ND - Not Determined

Those elements with no observable enrichment trends are:

Station HS	Station CS
Manganese	Titanium
Titanium	

No evaluation of calcium or lead enrichment was possible because of precipitation of insoluble sulfate salts in the WEP sample. This resulted from the use of sulfuric acid as the electrolyte in the collection device. However, calcium is enriched in the two cyclone ash fractions at each station and lead is enriched in all ash fractions except that of the largest HS particulates.

Calculation of enrichment was possible from the cyclone ash study, however an insufficient number of ash fractions was available for complete correlation of enrichment with particle size. An additional study of Andersen collected ash fraction was performed for that purpose.

6.3 Concentration and Enrichment Ratios of Andersen Cascade Impactor Samples

Based on the initial data from the cyclone train, nine trace elements were chosen for a follow-up enrichment study. Eight Andersen ash fractions plus the back-up WEP were analyzed for the following elements:

Arsenic
Cadmium
Chromium
Copper
Lead
Manganese
Nickel
Selenium
Zinc

These elements were selected to include those for which substantial evidence of enrichment has been shown or for which evidence of volatilization or oxide formation mechanisms exist to account for their enrichment. Mercury and fluoride were not included in this study due to insufficient ash sample.

The purpose of this part of the study was to define elemental concentration for a larger number of fly ash fractions, each representing a statistically smaller size range. Analytical results are found in Table 6 -4 and converted to enrichment ratios in Table 6-5. Several differences between the results from the two stations were observed.

Analysis of the Andersen samples shows that arsenic and selenium were more enriched in the fly ash exiting the hot-side precipitator. Though enriched in all fractions, the increased amounts as As and Se collected in the WEP sample appears to either be vaporous or of such small particle diameter that significantly more surface area was available for condensation than in the next size fraction.

The remaining seven elements of the study exhibited higher enrichment ratios for fly ash exiting the cold-side ESP. They included:

Cadmium
Chromium
Copper
Lead
Manganese
Nickel
Zinc

Cadmium is enriched only in the finest fraction at each plant. Chromium and manganese are enriched only in the finest fraction at Station HS while enriched in all fractions at Station CS. Lead is not enriched at Station HS and enriched in all fractions at Station CS. Again, no evaluation can be made for lead enrichment in the WEP sample.

TABLE 6-4. ANALYTICAL RESULTS OF ANDERSEN COLLECTED FLY ASH FRACTIONS

Fly Ash Size Fraction (μm)	Concentrations as μg/g										Ash Fraction Distribution (%)
	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	Ti	
Station HS:											
>8.0	64	7.0	125	265	235	112	49	110	135	8780	9.5
5.0-8.0	69	5.9	110	320	225	126	45	120	140	--	11.4
3.3-5.0	70	6.5	107	275	250	119	54	145	125	--	16.6
2.3-3.3	71	9.0	110	310	285	95	60	170	165	--	11.6
1.5-2.3	75	8.0	96	375	330	106	78	185	185	--	20.9
0.74-1.5	72	5.0	89	445	355	127	47	255	240	--	17.2
0.45-0.74	74	6.0	99	475	320	165	92	305	275	--	8.6
0.30-0.45	87	13	115	490	265	130	87	420	315	8080	2.7
<0.30 + Vaporous	695	51	515	1760	2420	295	--	8780	4250	(8430)**	1.6
Σ*	82	7.7	110	380	325	122	—	330	253	00	100.0
Ash Equivalent of Coal	15.6	11.7	182	182	312	91	87	15.6	152	8700	
Station CS:											
>8.2	33	4.0	225	330	630	155	140	59	365	8800	15.3
5.1-8.2	57	3.0	205	320	605	131	140	44	265	--	6.8
3.4-5.1	62	3.8	200	360	670	127	150	42	245	--	10.1
2.4-3.4	89	5.0	220	400	690	129	180	43	225	--	10.4
1.5-2.4	75	4.4	190	430	875	130	200	42	275	--	16.6
0.77-1.5	77	5.5	200	500	950	148	210	32	315	--	21.8
0.47-0.77	90	6.5	205	585	1070	148	220	31	600	--	13.2
0.32-0.47	140	5.5	340	600	1010	290	210	84	1290	9870	2.5
<0.32 + Vaporous	770	89	570	1140	1930	130	NA	3160	6200	(9430)**	3.3
Σ*	95	7.6	221	408	860	144		145	550		100.0
Ash Equivalent of Coal	34	6.1	114	123	298	45	103	15.8	57	8680	

All values represent the average of duplicate determinations.

*Mean concentration of flue gas particulate fractions determined by combining the individual concentrations in proportion to the ash distribution by Andersen collection

**Titanium values are the average of largest and finest Andersen ash fraction concentrations.

TABLE 6-5. ELEMENTAL ENRICHMENT RATIOS* OF ANDERSEN COLLECTED FLY ASH FACTIONS

Fly Ash Size Fraction (μm)	Concentrations as μg/g									Ash Fraction Distribution (%)
	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn	
Station HS:										
>8.0	4.1	0.6	0.7	1.4	0.8	1.2	0.6	7.0	0.9	9.5
5.0-8.0	4.4	0.5	0.6	1.8	0.7	1.4	0.5	7.2	0.9	11.4
3.3-5.0	4.5	0.6	0.6	1.5	0.8	1.3	0.6	9.4	0.8	16.6
2.3-3.3	4.6	0.8	0.6	1.7	0.9	1.0	0.7	11.0	1.1	11.6
1.5-2.3	4.8	0.7	0.5	2.0	1.1	1.2	0.9	11.8	1.2	20.9
0.74-1.5	4.6	0.4	0.5	2.4	1.1	1.4	0.5	16.3	1.6	17.2
0.45-0.74	4.7	0.5	0.5	2.6	1.0	1.8	1.0	19.5	1.8	8.6
0.30-0.45	5.6	1.1	0.6	2.7	0.8	1.4	1.0	27	2.1	2.7
<0.30 + Vaporous	44.6	4.4	2.8	9.7	7.8	3.2	--	563	30	1.6
Σ**	5.2	0.7	0.6	2.1	1.0	1.3	—	21	1.7	100
Station CS:										
>8.2	1.0	0.7	2.0	2.7	2.1	3.4	1.4	3.7	6.4	15.3
5.1-8.2	1.7	0.5	1.8	2.6	2.0	2.9	1.4	2.8	4.6	6.8
3.4-5.1	1.8	0.6	1.8	2.9	2.2	2.8	1.4	2.6	4.3	10.1
2.4-3.4	2.6	0.8	1.9	3.2	2.3	2.9	1.7	2.7	3.9	10.4
1.5-2.4	2.2	0.7	1.7	3.5	2.9	2.9	1.9	2.6	4.8	16.6
0.77-1.5	2.2	0.9	1.8	4.0	3.2	3.3	2.0	2.0	5.5	21.8
0.47-0.77	2.6	1.0	1.8	4.8	3.6	3.3	2.1	2.0	10.5	13.2
0.32-0.47	4.1	0.9	3.0	4.9	3.4	6.4	2.0	5.3	23	2.5
<0.32 + Vaporous	22	14.5	5.0	9.3	6.5	2.9	--	200	109	3.3
Σ**	2.8	1.2	1.9	3.7	2.9	3.2	--	9.2	9.7	100%

---

*Ratio of ash fraction concentration to ash equivalent concentration of coal

**Mean enrichment of flue gas particulate fractions determined by combining the individual values in proportion to the ash distribution by Andersen collection.

6.4 Enrichment Model

To evaluate the dependence of trace element concentration (enrichment) of fly ash on particle size, the results of this study have been compared with the volatilization/recondensation model reported by Davidson, Natusch, and Wallace (DA-105). This model assumes:

- elements are partially or totally volatilized during combustion
- volatile elements either partially or totally recondense or adsorb on entrained particles (fly ash) in the flue gas
- elements uniformly recondense or adsorb on all particles according to their available surface area
- specific surface area increases as particle size deminished due to the surface area to volume ratio
- fly ash particles are spherical in shape
- the concentration of an element in the bulk ash particle (excluding condensed contribution) is independent of particle size

If element X is uniformly deposited (condensed or adsorbed) on a spherical ash particle and also uniformly contained throughout the bulk particle, the total concentration for element X can be defined by the equation:

$$C_x = C_B + C_s \cdot SSA \qquad (6\text{-}3)$$

where,

C_x = total concentration of element x ($\mu g/g$)
C_B = bulk concentration of element x ($\mu g/g$)
C_s = surface concentration of element x ($\mu g/m$)
SSA = specific surface area of particle. (m^3/g)

For spherical particles specific surface area is defined as

$$SSA = \frac{A}{m} = \frac{A}{\rho V} = \frac{\pi D^2}{\rho \cdot 1/_6 \ \pi D^3} = \frac{6}{\rho D} \qquad (6\text{-}4)$$

where,

A = particle surface area
m = particle mass
ρ = particle density
V = particle volume
D = particle diameter

Assuming particle density is not a function of size, the total concentration of element x is proporational to the inverse diameter. By combining Equation 6-3 with Equation 6-4:

$$C_x = C_B + C_s \cdot \frac{6}{\rho D} \qquad (6\text{-}5)$$

$$C_x = C_B + K \cdot C_s \cdot D^{-1} \qquad (6\text{-}6)$$

For purposes in this study, the comparison of concentration versus inverse diameter is complicated by an additional variable - the difference in feed coal at each plant. Normalizing the ash concentrations to the coal ash concentration (formulization of enrichment ratios presented in Table 6-5) removes the effect of differing trace element concentrations in the feed coals. Since the enrichment ratio of an ash fraction is directly proportional to the concentration (Equation 6-2), enrichment is proportional to the inverse diameter.

$ER \propto D^{-1}$

Figures 6-7 through 6-15 are the resulting plots for the trace element enrichment data versus the inverse diameter of the Andersen cascade impactor ash fractions.

The diameter used in the plots is the geometric mean diameter. The geometric mean diameter in microns for each ash fraction j is obtained from the upper and lower D_{50} cut-off diameters of the Andersen plates:

$$\text{Geometric mean diameter} = D_{gm} = \sqrt{(D_{50j})\ (D_{50j-1})} \qquad (6\text{-}7)$$

For the largest fraction D_{50j} is determined from the largest particle observed in the SEM photographs. In the case of the finest fraction, D_{50j-1} is defined as one-half of D_{50j}. This assumption may cause less confidence in the diameter of the finest ash fraction than the other fractions. Therefore error ranges have been added to enrichment plots for the finest fractions.

A linear least squares fit of the enrichment data for each of the nine elements is also presented in enrichment plots. The fit includes all points except the finest (WEP) fraction, which has been omitted from the calculation due to the undetermined volatile element contribution which is independent of particle diameter. However, comparison of the observed enrichment of the WEP fraction with the value predicted from the linear least squares enrichment fit provides an estimate of volatile trace elements collected in the WEP sampler:

$$\%\ \text{volatile WEP} = \frac{\text{Enrichment (Measured-Predicted)}}{\text{Enrichment Measured}} \times 100 \qquad (6\text{-}8)$$

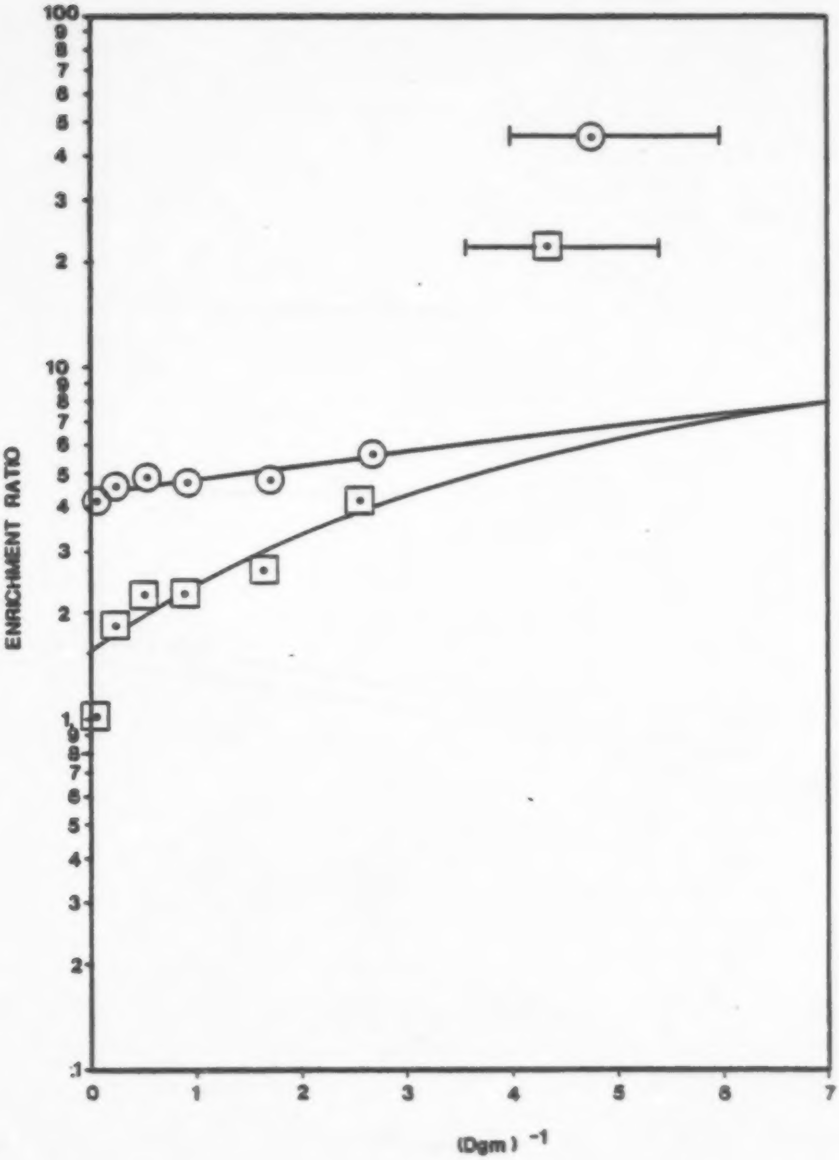

FIGURE 6-7

ARSENIC ENRICHMENT VERSUS DIAMETER^{-1}

⊙ HS

⊡ CS

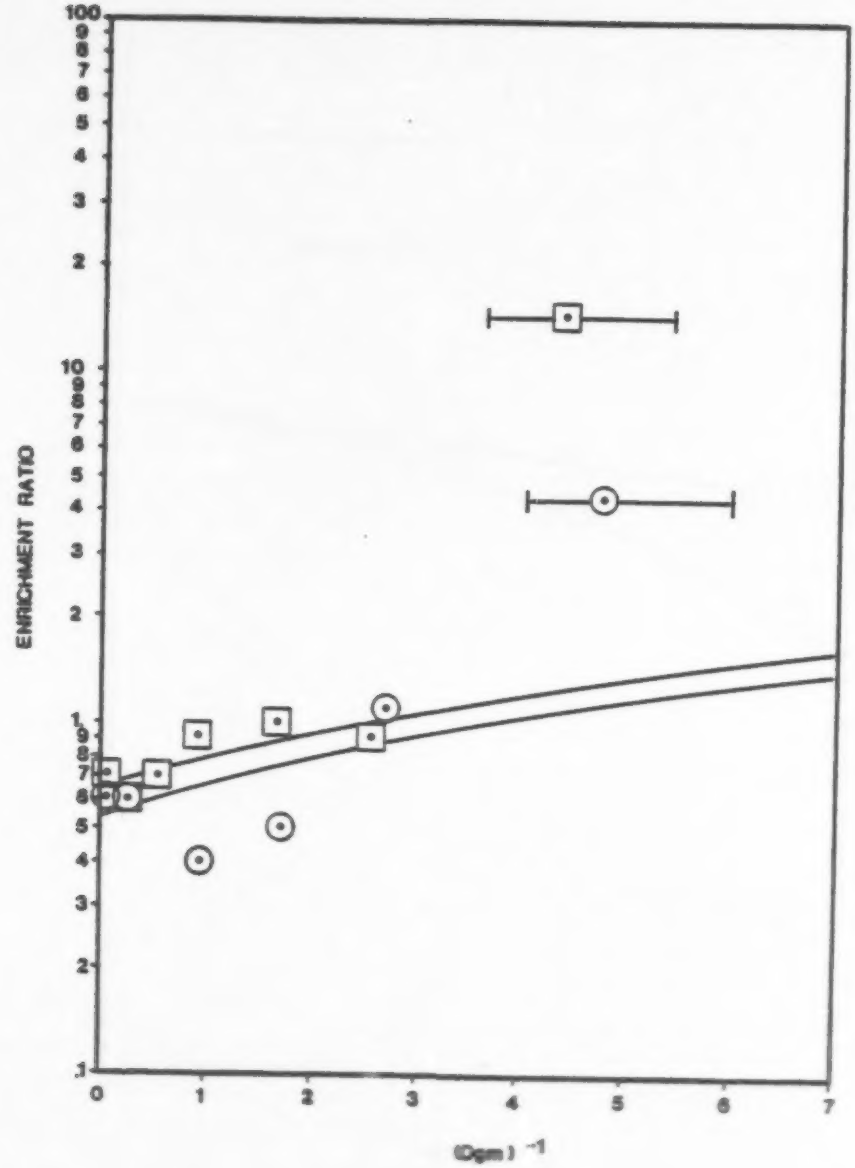

FIGURE 6-8

CADMIUM ENRICHMENT VERSUS DIAMETER^{-1}

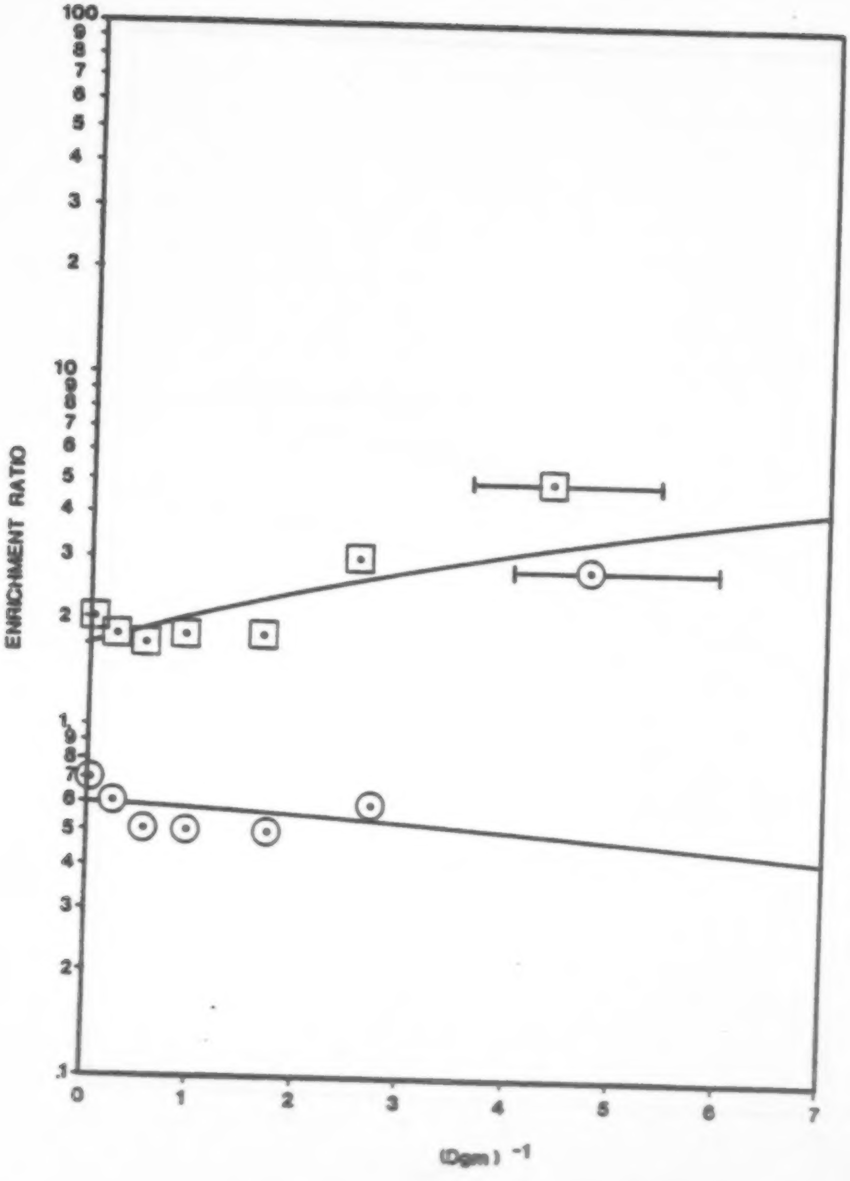

FIGURE 6-9

CHROMIUM ENRICHMENT VERSUS DIAMETER[1]

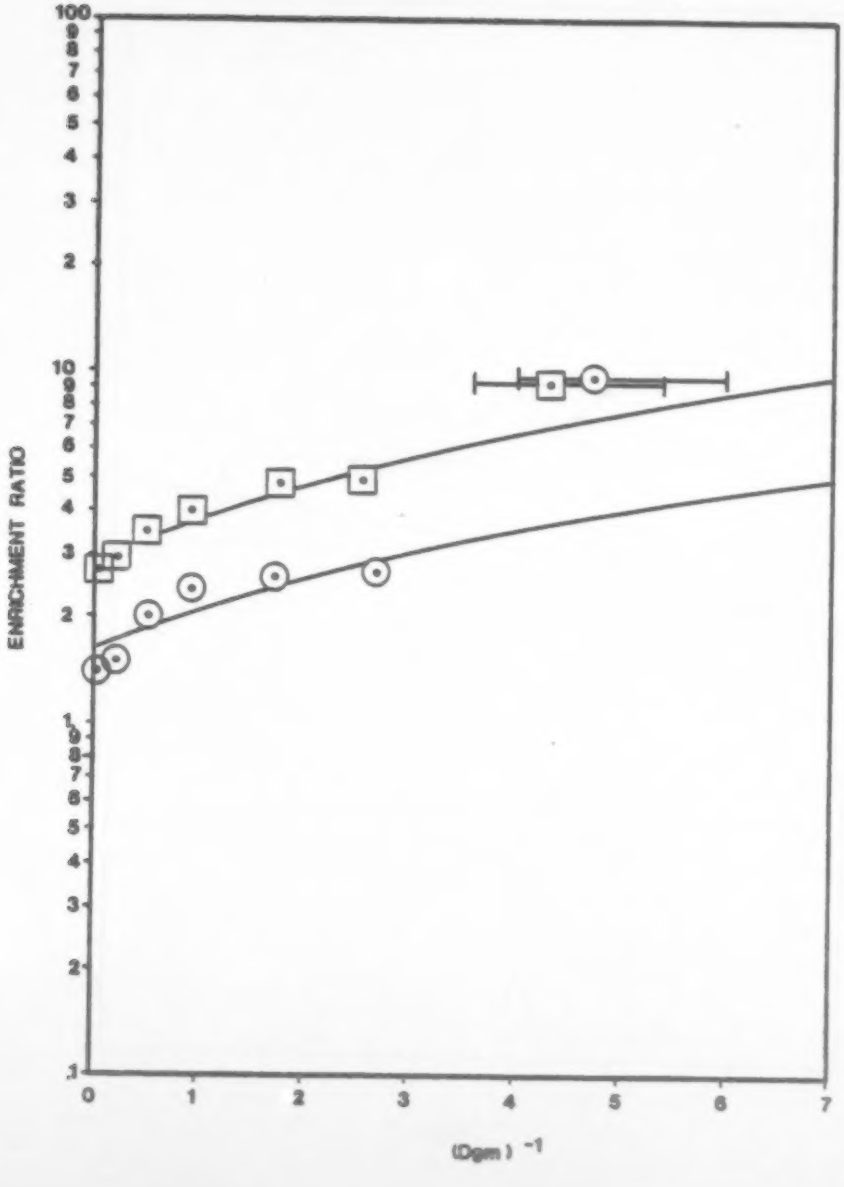

FIGURE 6-10

COPPER ENRICHMENT VERSUS DIAMETER^{-1}

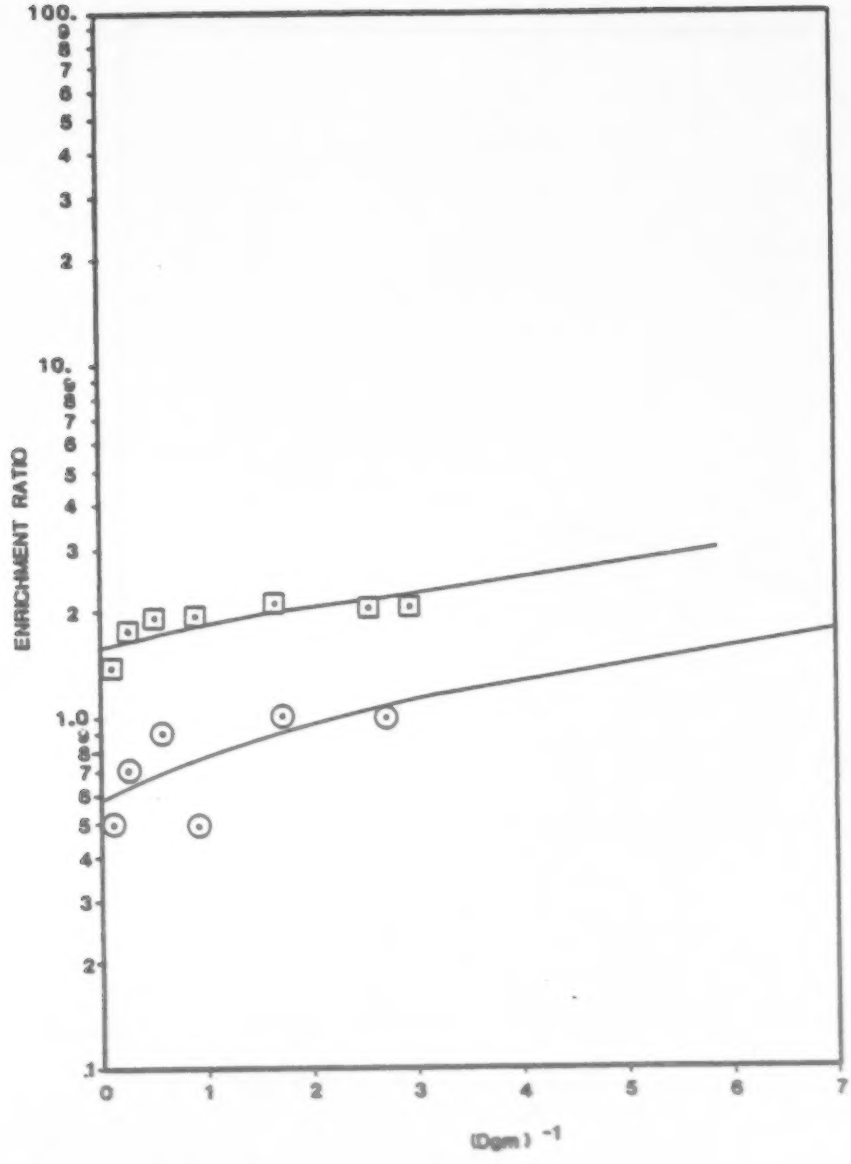

FIGURE 6-11

LEAD ENRICHMENT VERSUS DIAMETER

⊙ HS

⊡ CS

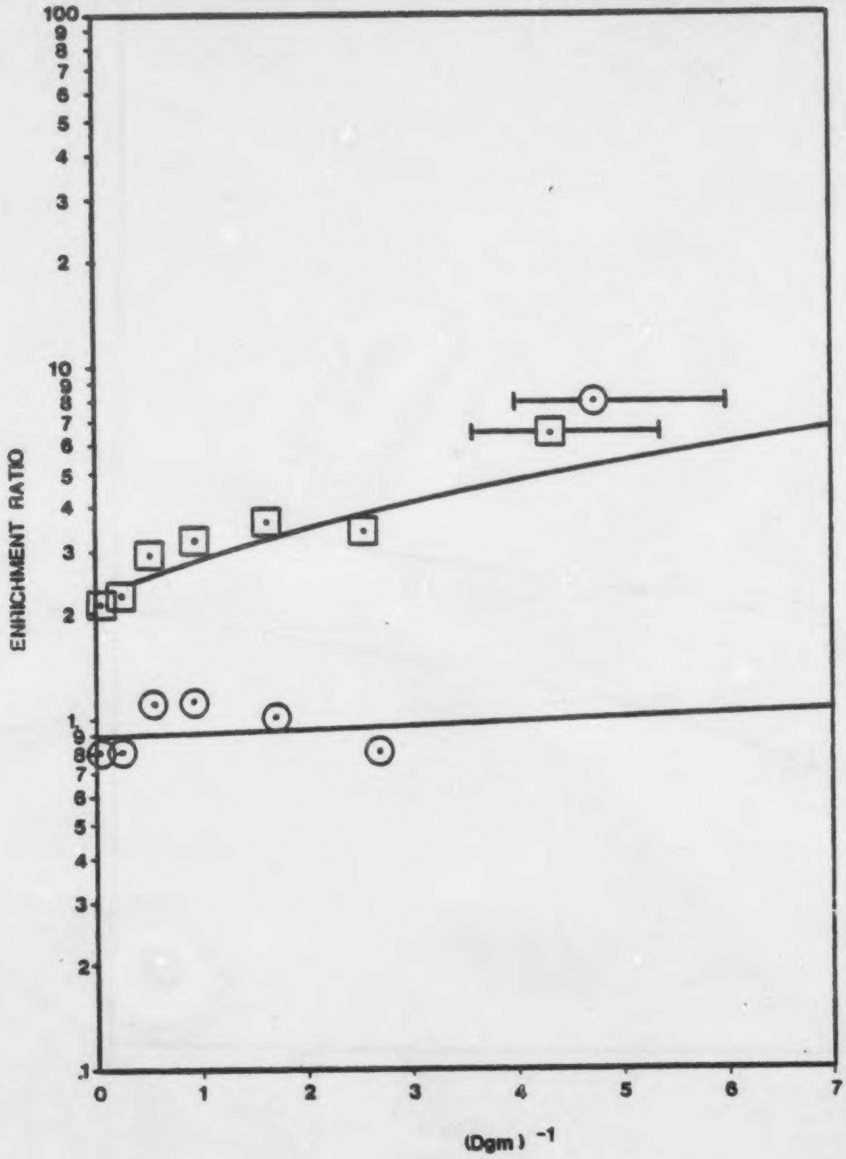

FIGURE 6-12
MANGANESE ENRICHMENT VERSUS DIAMETER^{-1}

⊙ HS

⊡ CS

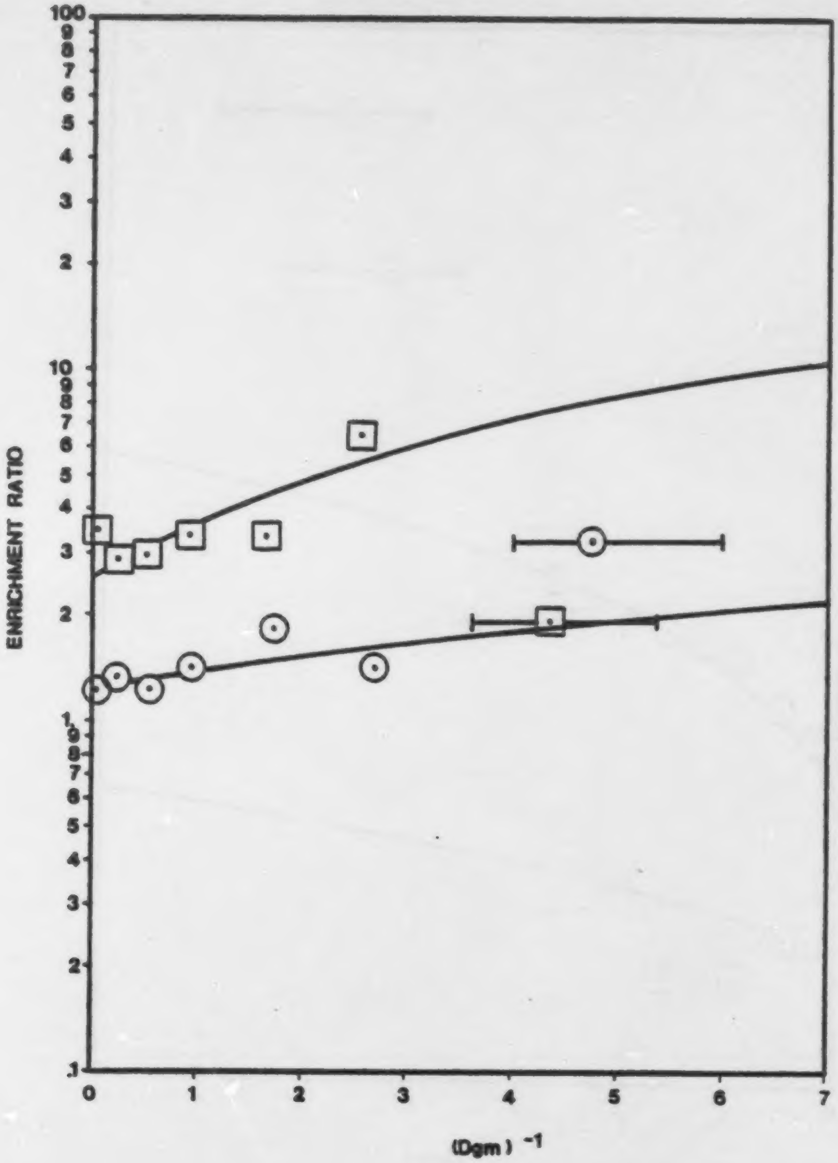

FIGURE 6-13
NICKEL ENRICHMENT VERSUS DIAMETER^{-1}

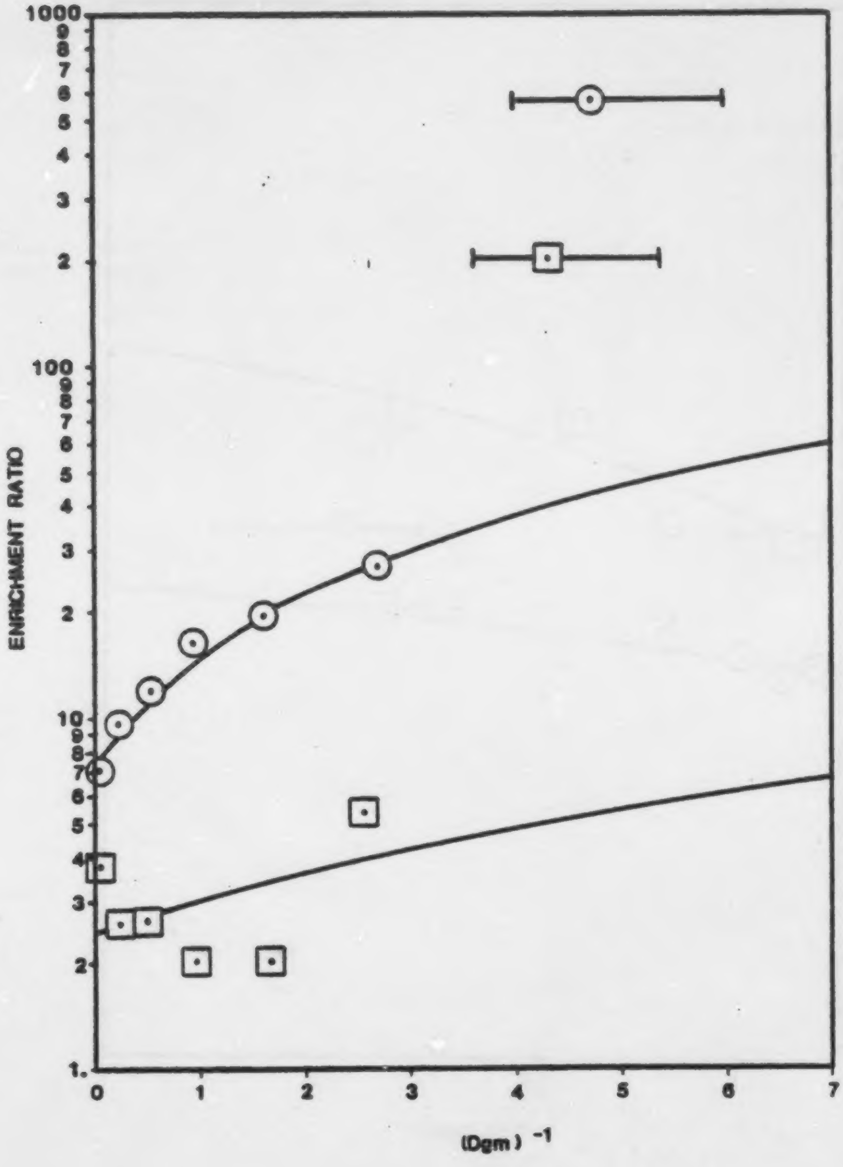

FIGURE 6-14
SELENIUM ENRICHMENT VERSUS DIAMETER^{-1}

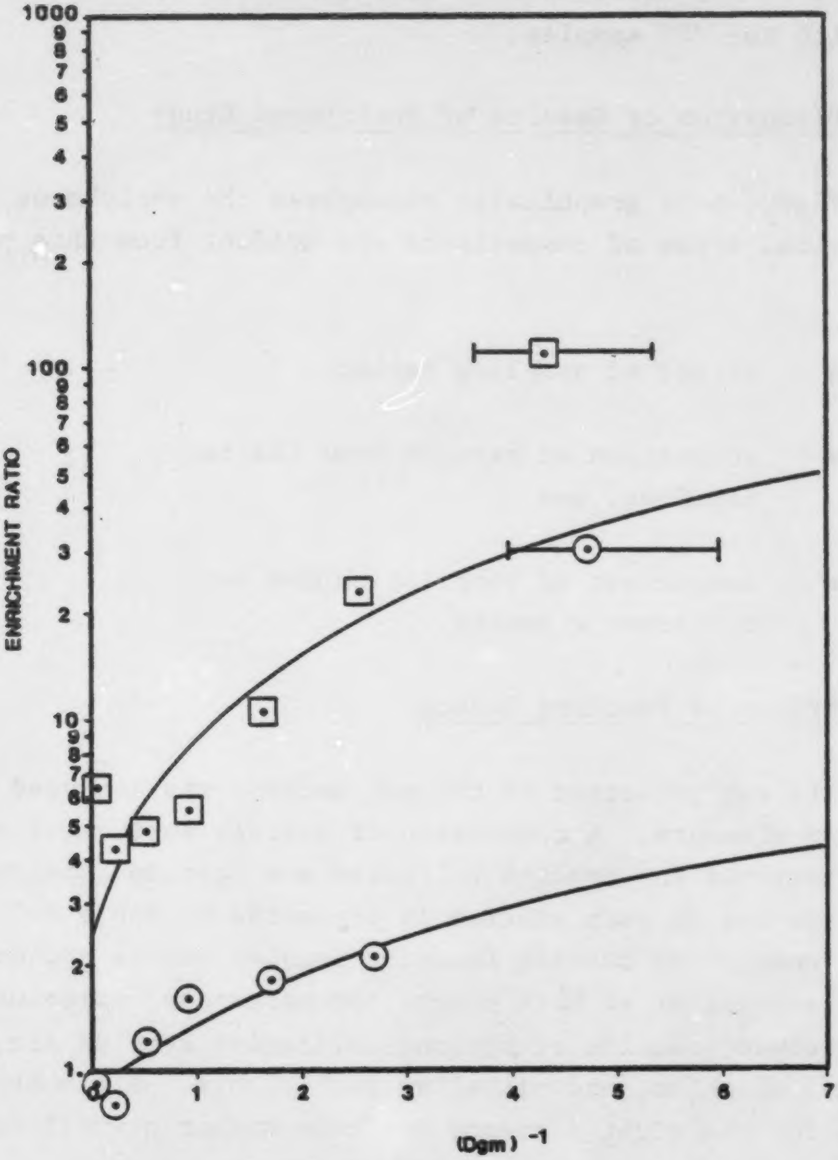

FIGURE 6-15

ZINC ENRICHMENT VERSUS DIAMETER^{-1}

⊙ HS

⊡ CS

Table 6-6 presents the volatile mass contribution for each element to the total element mass collected in the finest ash fraction with the WEP sampler.

6.5 Discussion of Results of Enrichment Study

Figure 6-16 graphically summarizes the enrichment study. Several types of comparisons are evident from this presentation:

- effect of sampling method,
- comparison of results from the two stations, and
- comparison of behaviors shown by different elements.

6.5.1 Effect of Sampling Method

Fly ash collected by the two methods was analyzed for eight common elements. A comparison of average enrichment of the fly ash determined for cyclone collected and cascade impactor collected samples at each station is presented in Table 6-7. Enrichment results of cascade impactor samples versus cyclone collection are higher at both plants for manganese, selenium, and zinc. Enrichment results of cyclone collection samples are higher for cadmium, chromium, and nickel at both plants. A comparison of results for the eight elements indicate higher overall enrichment by cascade impactor collection at the hot-side station and by cyclone collection at the cold-side station. However, at the 95% confidence level there is not a significant difference for all elements to indicate collector bias on the results.

TABLE 6-6. % VOLATILE TRACE ELEMENTS IN WET ELECTROSTATIC PRECIPITATOR COLLECTOR*

	HS WEP	CS WEP
As	86 (82-87)	77 (70-81)
Cd	58 (40-71)	91 (90-92)
Cr	76 (73-78)	33 (18-43)
Cu	62 (52-68)	27 (10-39)
Mn	87 (86-88)	28 (12-38)
Ni	42 (34-48)	**
Se	93 (90-94)	97 (96-98)
Zn	89 (86-92)	70 (58-78)

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*Determined by comparison of measured WEP enrichment with the enrichment model.

**Enrichment not detected.
Results indicate the analyzed value and range.

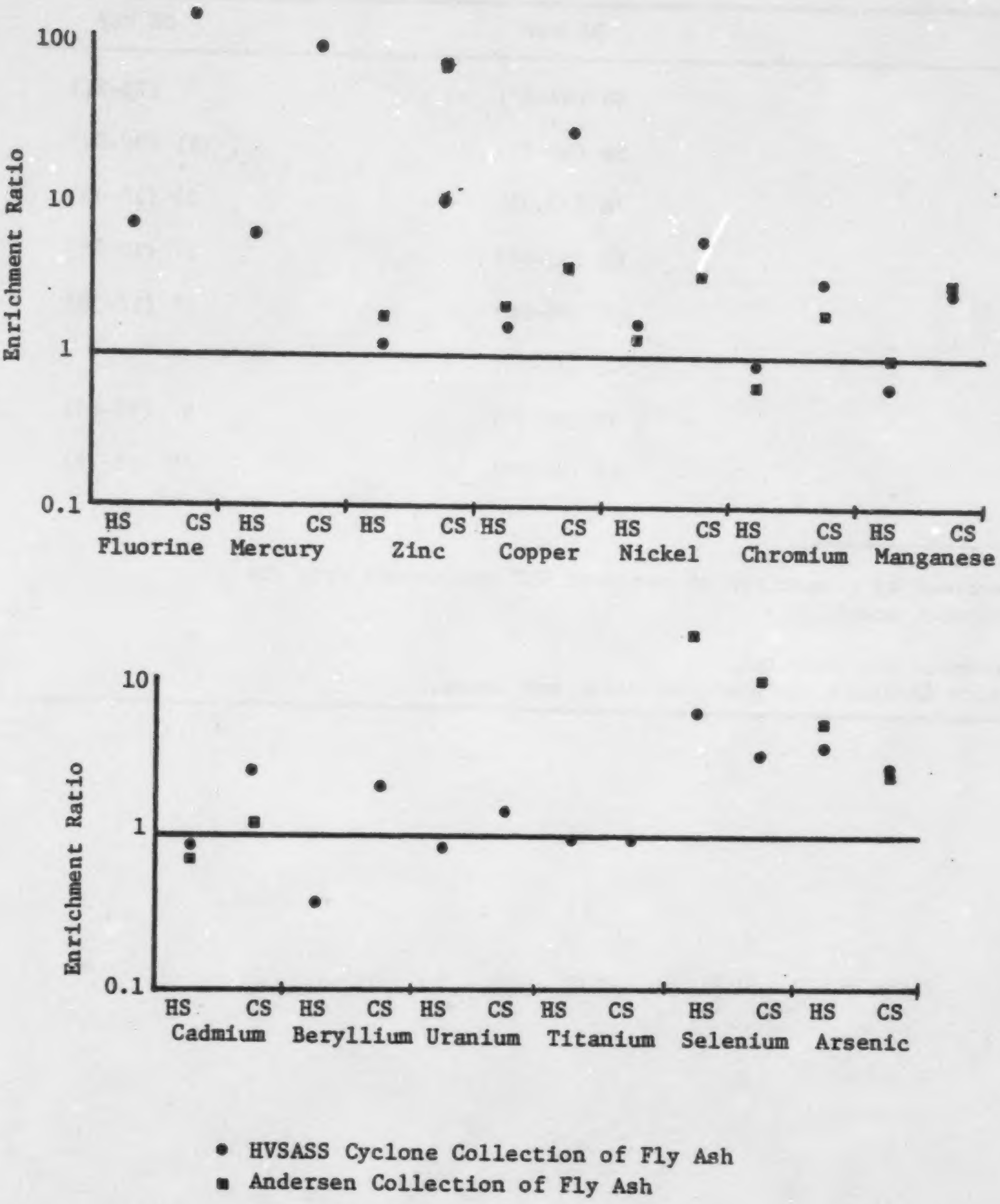

Figure 6-16. Average Enrichment of Fly Ash (Station HS vs Station CS)

TABLE 6-7. COMPARISON OF ENRICHMENT RESULTS OF CYCLONE AND CASCADE IMPACTOR SAMPLERS

	Enrichment Ratio			Enrichment Ratio		
Element	Cyclone	Cascade Impactor	Difference*	Cyclone	Cascade Impactor	Difference*
As	3.8	5.2	-.31	2.8	2.8	.00
Cd	.85	.70	+.19	2.6	1.2	+.74
Cr	.92	.60	+.42	3.1	1.9	.48
Cu	1.6	2.1	-.24	27.	3.7	1.52
Mn	.66	1.0	-.41	2.6	2.9	-.11
Ni	1.4	1.3	+.07	4.7	3.2	+.38
Se	6.3	21.	-1.08	3.3	9.2	-.94
Zn	1.2	1.7	- .34	72	109	-.41
		Mean ± 2 σ	- .21 ± .24			.20 ± .36

---

*$\frac{2(C-CI)}{(C+CI)}$

6.5.2 Comparison of Results for the Two Stations

The mean concentration of the elements studied in the flue ash particulate fractions indicated enrichment (i.e, enrichment factor >1.0). The following exceptions were noted at each plant:

Hot-Side Fly Ash		Cold-Side Fly Ash
Beryllium	Manganese	Titanium
Cadmium	Titanium	
Chromium	Uranium	

Fly ash exiting the cold-side ESP is generally more enriched for all elements. Noted exceptions to this trend were arsenic and selenium which exhibit higher enrichment in the hot-side fly ash. These two elements may partially condense prior to cold-side ESP particulate removal.

A definitive explanation of the observed enrichment phenomena is clouded by two conditions:

- difference in feed coals, and
- particulate loading of the flue gas exiting the precipitator.

Although the two sites were selected primarily with the particulate control device in mind, their use of similar feed coals was considered as well. Analysis of the two coals (both low sulfur sub-bituminous coal from Wyoming) identified different physical and chemical characteristics. Specifically, although the mineral and trace element content are similar, the distribution of trace elements with the organic/inorganic phase of the coal were quite dissimilar (Tables 5-1 and 5-4).

During the sampling periods the average particulate loading of the flue gas exiting the hot-side precipitator was almost five times higher than that of the cold-side ESP. This provided greater surface area for condensation to occur at Station HS, possibly diluting the condensation effect expected under ideal particulate removal operation.

6.5.3 Comparison of Elemental Behavior Between the Two Stations

Of the 15 elements in the study, all are discussed in this section:

Arsenic
Beryllium
Cadmium
Calcium
Chromium
Copper
Fluorine
Lead
Mercury
Manganese
Nickel
Selenium
Titanium
Uranium
Zinc

Lack of information for calcium and lead enrichment in the WEP prevent complete enrichment characterization.

Table 6-8 contains a summary of the behavior of the elements. Important observations listed there and discussed for each element in the following paragraphs include:

- coal comparison - highest trace element concentration.
- coal comparison - highest association of element in organic (ash-free) phase.

TABLE 6-8. COMPOSITE OF COAL AND FLY ASH TRENDS FOR ELEMENTS

Element	Highest Concentration In Coal	Highest Organic Association In Coal (HS/CS)	Average Fly Ash Enrichment† HS	Average Fly Ash Enrichment† CS	Enrichment All Fractions HS	Enrichment All Fractions CS	Enrichment WEP Fraction HS	Enrichment WEP Fraction CS	Progressive Enrichment with Fine Particulates HS	Progressive Enrichment with Fine Particulates CS
Arsenic	CS	CS (0/15)	E*	E	x	x	x	x	x	x
Beryllium	HS	CS (82/98)	D	E*			x	x		
Cadmium	HS	CS (0/65)	D	E*			x	x		x
Calcium	HS	HS (94/60)	ND	ND		ND	ND	ND		
Chromium	-	CS (67/87)	D	E*		x	x	x		
Copper	-	CS (18/37)	E	E*	x	x	x	x	x	x
Fluorine	-	CS (52/58)	E	E*	x	x	x	x	x	x
Lead	CS	CS (0/66)	ND	ND		ND	ND	ND		x
Manganese	CS	HS (78/75)	D	E*		x	x	x		x
Mercury	HS	CS (0/40)	E	E*			x	x		x
Nickel	HS	HS (89/82)	E	E*	x	x	x	x		
Selenium	CS	CS (10/56)	E*	E	x	x	x	x	x	
Titanium	CS	CS (32/73)	D	D*						
Uranium	CS	CS (63/71)	D	E*			x	x		x
Zinc	HS	CS (0/55)	E	E*		x	x	x		x

---

†E - Enrichment, D - Depletion, * Station with Higher Enrichment ND - Not Determined.

- fly ash comparison - enrichment or depletion of total flue gas particulate fractions and station with highest enrichment,
- fly ash comparison - enrichment of WEP (finest particulate and vapor) fraction, and
- fly ash comparison - identification of elements exhibiting progressive (or increased) enrichment from the larger to the finest particulate fractions.

Arsenic

Arsenic is enriched in all fly ash fractions at both stations. Corresponding fractions of the hot-side precipitator are more enriched than the cold-side fractions. This may be explained by condensation and subsequent removal of arsenic with the larger particulates in the cold-side precipitator. The Andersen results (Table 6-5) show progressive enrichment from the larger to finer particulates, with highest arsenic enrichment associated with the fine/vaporous fraction. This enrichment increase of the WEP fraction appears to result primarily from collected arsenic vapor exiting the hot-side and cold-side ESP's. Although associated with the inorganic phase of the coal, the cold-side coal has a slightly higher organic association (HS-0%, CS-15%). This association does not seem to greatly affect the enrichment results.

Beryllium

Beryllium enrichment is identified only in the WEP (fine ash and vapor fraction) for both stations in Table 5-3. Observing the lower total enrichment ratio for the hot-side ESP fly ash, less beryllium appears associated with Station HS fly ash. Although beryllium is found in higher concentration in the Station HS coal, this element displays higher organic association in CS Coal (98% compared to 82% in HS Coal). This organic association may account for greater Be enrichment levels in Station CS fly ash, since organically associated elements may be more likely volitalized during combustion than elements bound in the mineral phase.

Cadmium

The results for cadmium are similar to beryllium. Andersen collected ashes show a depletion of cadmium in the larger fractions. This is also true for cyclone collected ash except for the largest fraction at Station CS. Increased cadmium enrichment is observed in the finest fraction at each station, with higher enrichment at Station CS. While a higher concentration was noted for HS Coal (HS, 0.90; CS, 0.70 ppm), the degrees of organic association in the two coals are quite different (HS - 0%, CS - 65%). The higher organic association of cadmium in CS Coal is identified with increased volatilization and subsequent enrichment of the finest fractions.

Figure 6-8 shows higher enrichment of cadmium at the cold-side station. The deviation of the WEP concentrations from the extrapolation of particulate fraction results indicate that most of the cadmium collected by the WEP is in the vapor state (58% at Station HS and 91% at Station CS).

Calcium

Calcium enrichment of fly ash was found at both plants (Table 6-3). Although not usually considered by most investigators as an element displaying enrichment, results of a three station study (RA-219) identified higher calcium content in the flue gas than anticipated by from the ash content.

	Flue Gas Ash Distribution (%)	Flue Gas Ca Distribution(%)
Station I	.3	.85
Station II	.7	.8
Station III	12.9	16.6

Calcium is associated with the organic phase in both coals (HS-94%, CS-60%); with the stronger association in the hot-side coal. Insufficient results prevent the comparison of phase association with enrichment.

Chromium

Station HS Andersen fractions are depleted in chromium with exception of the WEP (fines and vaporous). All fractions at Station CS are enriched. The chromium content of the two coals are almost equivalent; however, again for CS Coal, chromium is more organically associated (HS - 67%, CS - 87%). The enrichment curves presented in Figure 6-9 support the chromium enrichment of ash fractions from cold-side collection, and chromium depletion in the hot-side ash fractions. Estimation of possible vapor contribution to the hot-side WEP collector was 76%.

Copper

All ash fractions are enriched in copper, and a progressive increase in enrichment is noticed from the larger to the finer particulates. Total enrichment is higher at Station CS and condensation of copper on ash particles is the expected mechanism at both plants. From Figure 6-10 the volatile contribution to the WEP is more significant at the hot-side station (62% at Station HS and 27% at Station CS). Equal concentrations of copper are found in the two coals, yet in Coal CS, the copper is more organically associated (HS - 18%, CS - 37%). Organic association of the element is noted with higher enrichment of the resulting fly ash.

Fluorine

Fluorine is enriched in all cyclone ash fractions. A surprising observation is the very high fluorine content of the finest CS fraction (Table 6-3). Although this WEP collected fluoride is assumed to be vaporous, the increased amount at Station CS is unexplained. Inlet fluorine content of the coals is approximately equal, and organic association of CS Coal is slightly higher (HS - 52%, CS - 58%). The increased content of fine particulate and vapor phase fluorine at the cold-side station is noted with only slightly higher organic association with the feed coal.

Manganese

Andersen collected fly ash from Station CS is enriched in all fractions and progressive enrichment of manganese is observed in the finer ash particles (Figure 6-12). The finest ash fraction at each station is enriched; however, the larger particles at Station HS are depleted in manganese and no strong enrichment trend with particle size is identified. Enrichment by condensation is apparent at Station CS (Figure 6-12); however, the high enrichment of the fines and depletion of larger particles at Station HS are not indicative of condensation. Eighty-seven percent of the manganese present in the hot-side WEP is estimated to be vaporous (28% at Station CS). Manganese concentration is higher in Coal CS and both coals have approximately equal association of manganese with the organic phase (HS - 78%, CS - 75%).

Mercury

Mercury is primarily associated with the WEP collected fraction. Vapor phase presence of mercury has been documented in past studies (BI-060, DI-043). A lower vapor phase mercury emission was identified with both plants in this study than the reported emission of 90% total inlet mercury with the flue gas in the above studies. The mercury in Coal CS is more organically associated (HS - 0%, CS - 40%) and resulting fly ash is more enriched.

Nickel

All ash fractions are enriched in nickel with the cold-side ash exhibiting predominantly higher enrichment. Enrichment curves (Figure 6-13) indicate the WEP samples do not fit the model. Approximately 40% of the nickel in HS WEP appears to be vaporous. The WEP sample for Station CS contains approximately one-third the expected nickel content.

Lead

Lead is more enriched in cold-side ash fractions. Both the lead content and organic phase association of the lead are higher for CS Coal. Higher enrichment of the cold side ash fractions are the result of condensed vaporous lead. No estimation of volatile lead in flue gas was possible for the two stations.

Selenium

Selenium is primarily associated in the vapor phase, with partial condensation on ash particles at Station HS

(Figure 6-14). Station CS ash displays no strong enrichment trend in the Andersen particulate fractions, yet the follow-up WEP collector is highly enriched in selenium. The higher enrichment of larger ash fractions (>2 μm) as compared to .5-1 μm, identifies possible condensation of selenium prior to particulate removal by the ESP and subsequent removal of selenium with the precipitator ash. Organic association is more pronounced for Coal CS (HS - 10%, CS - 56%).

Titanium

Titanium exhibits no enrichment in the cyclone collected ash fractions. However, no noticeable depletion is observed. This is consistent with previous findings (RA-219) in which the titanium distribution was similar to ash distribution at Station HS.

	Ash Distribution (%)	Ti Distribution (%)
Bottom Ash	22.2	21.1
Precipitator	77.1	78.3
Fly Ash	0.7	0.6

Titanium of Coal CS is more organically associated (A - 32%, B - 73%); however, this association, as well as cooler temperature of the ESP, does not affect distribution of this element.

Uranium

Analysis of cyclone fractions resulted in enrichment of all ash fractions at Station CS and only the finest fraction at Station HS. Total enrichment of flue gas particulate fractions at the lower temperature of Station CS was approximately twice that of Station HS. Uranium in Coal CS has a slightly higher organic association (HS - 63%, CS - 71%) and Coal CS uranium concentration was roughly twice that of Coal HS. The enrichment factor normalizes that increased coal concentration, so it appears uranium associated with the organic fraction is condensing on ash particles.

Zinc

Zinc, though depleted in the large particles at Station HS, displays a progressive increase in enrichment with decreasing particle size at both stations. Higher total flue gas enrichment is noted at Station CS. The zinc content of Coal HS was twice that of Coal CS. The association of zinc with the ash-free coal fraction (organic) was more pronounced for Coal CS (HS - 0%, CS - 55%). The observed progressive enrichment is indicative of condensation. However, the increased enrichment of the finest fraction at each station appears to be higher than anticipated from condensation. In Figure 5-14, this increase of zinc content of the WEP fractions when compared with the expected value suggests that the following percentage of that fraction is vaporous:

Hot-Side WEP fraction - 89%
Cold-Side WEP fraction - 70%

7.0 TRACE ELEMENT EMISSIONS

A comparison of the emissions of the two electrostatic precipitators was performed to compare total trace element emissions and potential volatile emissions. Tables 7-1 and 7-2 present the comparative results.

7.1 Total Trace Element Emissions

Total trace element emissions for each element were calculated based on cyclone collected ash distribution, average particulate loading, and flue gas flow rate. The emissions in terms of lb/10^5 tons dry coal are presented in Table 7-1 In general, emissions are higher at the hot-side station due to the higher particulate loading. Exceptions are copper, fluorine, mercury, and zinc. These four elements are more organically associated in the cold-side coal indicating a possible correlation between organic association and enrichment.

For several elements significant amounts (>40%) of the element's total emission are in the WEP fraction associated with the cyclone collection system. The WEP fraction contains both volatile elements and the finest particulate fraction. Those elements with significant emissions in the finest ash fraction include:

Station HS
Beryllium
Cadmium
Fluorine
Mercury

Station CS
Beryllium
Cadmium
Chromium
Copper
Fluorine
Mercury
Nickel
Selenium
Zinc

TABLE 7-1. STACK EMISSION OF ELEMENTS DETERMINED FROM CYCLONE COLLECTION

Fly Ash Fraction	Concentration as lb/10^5 Tons Dry Coal													
	As	Be	Cd	Cr	Cu	F	Hg	Mn	Ni	Se	Ti	U	Zn	Ash
Station HS:														
Cyclones 1 & 2 (2.0μ)	15.5	0.80	1.3	40	63	230	0.064	51	27	16	2190	2.6	32	2.67×10^5
Cyclone 3 (0.8μ)	7.2	0.28	1.1	13	42	115	0.013	28	12	9.5	910	1.1	26	1.16×10^5
WEP (<0.8μ + Vaporous)	1.5	1.00	1.6	15	15	1370	4.0	5.0	12	15	170	0.41	14	2.11×10^4
Total Emission	24	2.1	4.0	68	120	1715	4.0	84	51	40	3300	4.1	72	4.04×10^5
Total Inlet with Coal	240	210	180	2800	2800	10400	28	4800	1400	240	1.3×10^5	180	2300	1.54×10^7
Station CS:														
Cyclones 1 & 2 (1.9μ)	2.1	0.14	0.21	6.5	5.8	16	0.003	15	3.2	0.51	195	0.51	6.1	2.45×10^4
Cyclone 3 (0.9μ)	2.6	0.13	0.08	5.6	10.0	28	0.003	24	3.0	0.72	220	0.55	7.6	2.49×10^4
WEP (<0.9μ + Vaporous)	1.0	0.65	0.65	8.8	182	3620	4.9	6.9	6.6	1.9	86	0.42	230	1.02×10^4
Total Emission	5.7	0.92	0.94	21	198	3660	4.9	46	13	3.1	500	1.5	244	5.96×10^4
Total Inlet with Coal	780	170	140	2600	2800	10800	22	6800	1020	360	2.0×10^5	400	1300	2.28×10^7

7.2 Volatile Trace Element Emissions

Although volatile trace element content of the flue gas was not measured directly, an estimation was made of the volatile contribution to the wet electrostatic precipitator. Since limited data appears in the literature, estimated volatile emissions have been reported in this section. Ranges have been assigned to identify uncertainties in the values.

Based on the enrichment versus particle size correlations (Figures 6-7 to 6-15) the volatile contribution to the Andersen associated WEP was estimated for 8 elements. Table 6-6 presented estimates of the fraction of the elements in the WEP which were collected as vapors in the flue gas. In Table 7-2 these vaporous emissions are presented as the estimated fraction of each element entering with the coal which is exiting the stack as a vapor. This method of presentation normalizes the different coal compositions and facilitates comparison.

Table 7-2. ESTIMATED VOLATILE TRACE ELEMENT EMISSIONS FROM IMPACTOR COLLECTION

	Hot-Side Station (Amount %)	Cold-Side Station (Amount %)
As	1.6 - 1.7	.19 - .22
Cd	.08 - .13	.16 - .16
Cr	.09 - .10	.01 - .03
Cu	.22 - .29	.01 - .05
Mn	.3 - .31	.024 - .076
Ni	.051 - .072	**
Se	.22 - .24	2.5 - 2.5
Zn	1.16 - 1.24	.83 - 1.1

(*) Ratio of mass of element volatile in flue gas to mass of element entering with feed coal.

** No volatile contribution observed.

8.0 Control Effectiveness at Each Station

To evaluate the removal efficiency of a control device (ESP), the inlet and outlet gas streams must both be characterized. In this study, the inlet gas streams to the ESP's were not sampled. Therefore, the collection efficiency of the control device cannot be determined.

However, with the feed coal characterization at each plant, the total plant collection (removal) efficiency can be defined.

Table 8-1 presents the collection efficiency of each plant defined by identifying total emissions from each plant and the total inlet with the feed coal (from Table 7-1) under the operation conditions of each plant during the sampling period.

Emissions at each plant during the sampling period are not necessarily representative of maximum control device (ESP) collection efficiency.

TABLE 8-1. CONTROL EFFICIENCY OF TRACE ELEMENTS (%)

Element	Hot-Side Station	Cold-Side Station
As	90.0	99.3
Be	99.0	99.4
Cd	97.8	99.3
Cr	97.6	99.2
Cu	95.7	92.9
F	83.5	66.1
Hg	85.7	77.7
Mn	98.2	99.3
Ni	96.4	98.7
Se	83.3	99.1
Ti	97.5	99.8
U	97.7	99.6
Zn	96.9	81.2
Ash	97.4	99.7

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APPENDIX A

SAMPLING

1.0 INTRODUCTION

Two coal-fired boilers were selected for study to define the occurrence and distribution of trace elements as a function of particle size in the fly ash emitted from the units. The two facilities selected have the same boiler configuration and are fired with similar coals. They differ in the placement of their electrostatic precipitators (ESP) relative to the combustion air preheaters. Station HS has a "hot-side" ESP; that is, the precipitator is upstream of the combustion air preheater. Station CS has the ESP positioned downstream of the combustion air preheater; this is known as a "cold-side" ESP. As the initial task of this program, Radian personnel sampled Station HS during the period September 2-16, 1976 and Station CS during the period September 20 - October 1, 1976.

Fly ash emitted from the plant stack was collected by size fractions using three different methods. In addition samples of the coal were collected. Analysis of these samples provided data to study the distribution of trace elements as a function of particle size and also provided information on the probable mechanisms of trace element inclusion in the emitted particles.

The following sections describe the facilities sampled, the sampling techniques utilized, and the flow rate measurements performed.

2.0 PLANT DESCRIPTION - STATION HS

Station HS consists of two 350 MW tangentially-fired boilers. The newer of the two units, Unit 2, was sampled. Hot-side electrostatic precipitators, upstream of the combustion air preheaters, designed for flow rates equivalent to 350 MW at an inlet gas temperature of 830°F are used for fly ash control. The boiler is fired with sub-bituminous coal transported by rail from Wyoming, where it is strip mined. The coal typically contains 30% moisture, 5% ash, 0.5% sulfur and 33% volatile matter and has a heating value of 8400 Btu/lb. The coal is initially stored in open piles from which it is conveyed to five storage silos. Coal from the silos is fed to the mills where it is pulverized prior to delivery to the boiler through a pneumatic conveying system.

Pyrites from the mills, economizer ash and bottom ash are sluiced alternately to an ash pond at approximately 4-hour intervals. The ash collected in the electrostatic precipitators is transferred to an ash storage silo by a pneumatic conveyor system and removed from the plant site by truck. Flue gas exits the system through a 500-foot stack, approximately 25 feet in diameter.

A schematic of the station with all sampled streams is presented in Figure A-1.

2.1 Plant Operation During Sampling

During the sampling period the boiler load varied from 290-355 MW operating essentially at full load during most of the period. The electrostatic precipitator performance was not consistent throughout the sampling effort. Particulate loading ranged from 0.03 gr/scf to 0.12 gr/scf.

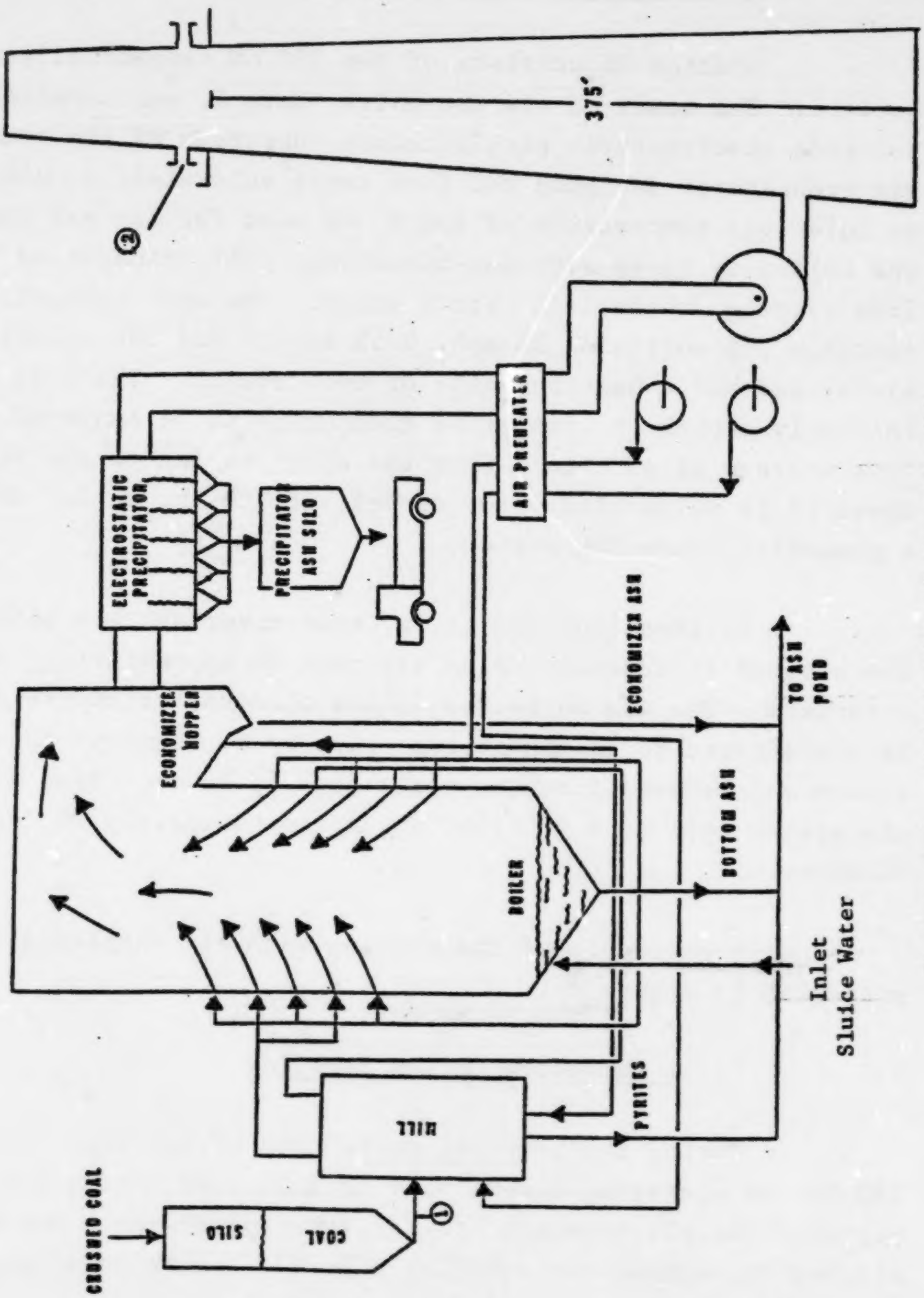
CRUSHED COAL
COAL SILO
①
MILL
PYRITES
BOILER
ECONOMIZER HOPPER
ELECTROSTATIC PRECIPITATOR
PRECIPITATOR ASH SILO
AIR PREHEATER
ECONOMIZER ASH
BOTTOM ASH
TO ASH POND
Inlet Sluice Water
②
375'

Figure A-1. Schematic of Station HS

2.2 Description of Sampling Points

The sample point locations for coal and flue gas are indicated in Figure A-1. The following section gives descriptions of the sampling points and the sampling techniques used at these points. Table A-1 shows the dates on which each type of sampling was conducted.

2.2.1 Coal

Five coal feeders (A through E) meter the coal from the five overhead storage silos to their respective mills for pulverization prior to being fed to the boiler. A coal sample was collected daily for eight days. The feeders A through E were sampled sequentially so that the total sample was a compositie of the coal being fed from all of the silos. The samples were collected by passing the container through the stream of coal falling from a conveyor in the feeder to the mill. Each of the daily samples were stored in one-liter polyethylene containers. The analytical sample resulted from the combination of daily samples.

2.2.2 Fly Ash

Fly ash exiting the 500-foot stack in the flue gas stream at Station HS was sampled through ports located at the 375-foot level, where a work platform was located. The internal diameter of the stack at this height is 25 feet. The average flue gas temperature was 315°F.

The sample ports were greater than 10 stack diameters downstream from the point of entry of the flue gas and therefore provided a good test plane at the port level. The stack was equipped with four ports 90° apart, 4 inches in diameter. In

TABLE A-1. Sampling Schedule at Station HS

Type of Sampling	Location*	9/2	9/3	9/4	9/5	9/6	9/7	9/8	9/9	9/10	9/11	9/12	9/13	9/14	9/15	9/16
Grain Loading	2	●		●		●	●	●	●	●	●	●		●	●	
Andersens	2		●	●		●	●	●	●	●	●	●		●	●	
One acfm Cyclones	2						●	●	●		●	●		●	●	
HVSASS Cyclones	2						●	●	●							
Coal	1							●	●	●	●	●	●	●	●	

*Location as noted in Figure A-1.

addition, there were two 10-inch ports 4 feet above the level of the 4-inch ports.

Velocity and grain loading measurements were taken at the south port using four traverse points. These points were selected by dividing the cross-sectional area of the stack into four equal-area concentric circles and finding the centroid of the south half of each circle as described in EPA Method 1. The distances from the inner stack wall for the four points were:

- 10 inches,
- 2 feet 7 inches,
- 4 feet 10 inches, and
- 8 feet.

Velocity measurements were taken daily during sampling. The average velocity was found to be 61 fps. The velocity traverses were used to determine the conditions necessary for isokinetic sampling and to determine the total gas flow through the stack.

Particulate loading determinations were made on 11 days during the sampling period with in-stack Gelman filters. These determinations were made by sampling an equal time at each of the four points. Thus, the particulate loading value determined is the average of points sampled. The results of each grain loading determination are given in Table A-2.

The moisture content of the gas stream was determined by condensing the moisture in a series of Smith-Greenburg impingers, them passing the gas through an impinger containing dry preweighed silica gel. The moisture content of the gas was calculated to be 12.1% based on the weight of water removed and the total volume of gas metered.

TABLE A-2. GRAIN LOADING DATA FOR STATION HS

Date	Grain Loading in gr/scf*
9/2/76	0.028
9/4/76	0.094
9/6/76	0.094
9/7/76	0.093
9/8/76	0.088
9/9/76	0.072
9/10/76	0.080
9/11/76	0.060
9/12/76	0.040
9/14/76	0.039
9/15/76	0.055
Mean ± std. deviation	0.068 ± .024

*60°F, 1 ATM.

2.3 Flow Rate Measurements

The following section describes the methods used to determine the flow rates of the individual streams at Station HS.

2.3.1 Coal

Coal is fed from the storage silo to the mills by a series of four feeders. The total throughput of each feeder in 100-pound units is indicated in the control room. Readings from these feeders were taken at the beginning and end of each day's sampling; thus, the total amount of coal fed to the boiler could be determined as a function of time. The coal feed rate for Unit 2 was determined to be 2.6×10^5 lb/hr moisture-free coal.

2.3.2 Fly Ash Flow Rate

The flow rate of flue gas from Station HS was determined to be 1.8×10^6 ACFM using the gas velocity (61 fps) and the cross-sectional area of the stack at the test plane. The flow rate of fly ash was determined using the average grain loading and the flue gas flow rate. The average fly ash flow rate was 5.2×10^2 lb/hr.

3.0 PLANT DESCRIPTION - STATION CS

Station CS consists of four 500 MW boilers of which Unit 1 was sampled. The plant design has electrostatic precipitators located downstream of the combustion air preheaters, hence the term cold-side precipitator. Each boiler is fired with sub-bituminous coal which is mined near the plant and transported by truck to the plant site. The coal has an average heat content of 9700 Btu/lb and contains approximately 19% moisture, 10% ash and 0.6% sulfur. The coal trucked into the plant is initially stored in piles at the plant site. Storage silos are filled from these piles by conveyor. The coal from the silos is fed to mills where the coal is pulverized and then pneumatically conveyed to the boiler.

Pyrites from the coal mills, economizer ash and bottom ash are sluiced simultaneously to a dewatering system approximately three times per shift. Ash collected in the electrostatic precipitator is pneumatically conveyed to a storage silo. This ash is taken from the plant site by truck. Flue gas exits the plant through a 500-foot stack which is approximately 24 feet in diameter.

A schematic of the station with the two sampled streams indicated is presented in Figure A-2.

3.1 Plant Operation During Sampling

During the sampling period, the boiler load on Unit 1 varied from 380-510 MW operating essentially at full load during the majority of the sampling period. For the first week of sampling, the precipitator was operated at peak efficiency. The grain loading was quite low, ranging from 0.008 gr/SCF to 0.022 gr/SCF. During the remainder of the sampling effort, the precipitator was not operated at peak efficiency, allowing collection of particulate samples at a faster rate.

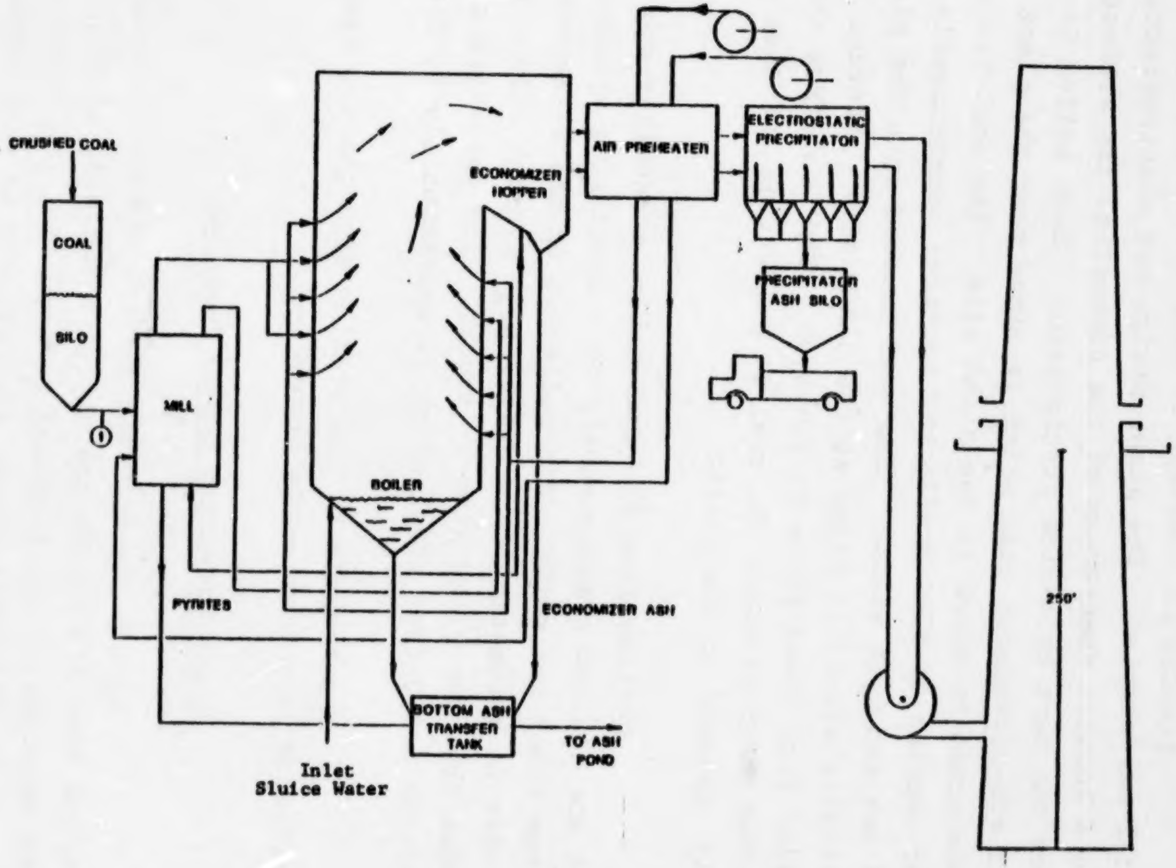
CRUSHED COAL
COAL
SILO
MILL
PYRITES
Inlet
Sluice Water
BOILER
ECONOMIZER
HOPPER
ECONOMIZER ASH
BOTTOM ASH
TRANSFER
TANK
TO ASH
POND
AIR PREHEATER
ELECTROSTATIC
PRECIPITATOR
PRECIPITATOR
ASH SILO
250'

Figure A-2. Schematic of Station CS

3.2 Description of Sampling Points

The sampling locations are schematically identified in Figure A-2. The following sections describe the sampling points and the manner in which each sample was collected. Table A-3 shows the dates on which each type of sampling was conducted.

3.2.1 Coal

Five coal feeders (A through E) meter the coal flow from the storage silos to their respective mills for pulverization prior to pneumatic transfer to the boiler. The coal feeders were sampled sequentially daily by station personnel passing a container through the coal stream falling from a conveyor. These samples were stored in one-liter polyethylene containers. A composite coal sample was formed by combining these samples.

3.2.2 Fly Ash

Fly ash was collected from the flue gas leaving Station CS through the 500-foot stack. The sampling station was located at the 250-foot level on a platform between the inner and outer walls of the stack. The internal diameter of the stack at this height is 24 feet. The average temperature of the flue gas was 220°F. The distance between the inner and outer walls of the stack is approximately 4 feet. This distance prevented traversing during sampling since a probe of sufficient length could not be inserted through the sampling ports.

The sample ports were located more than 10 stack diameters downstream of the entrance of the stack. Therefore, the sampling location provided a good test plane. The sampling location was equipped with four ports 90° apart. Each of these

TABLE A-3. Sampling Schedule at Station CS

Type of Sampling	Location*	9/20	9/21	9/22	9/23	9/24	9/25	9/27	9/28	9/29	9/30	10/1
Grain Loading	2		●	●	●	●	●	●	●			
Andersens	2		●	●	●	●	●	●	●	●	●	●
One acfm Cyclones	2		●	●	●	●	●	●	●	●	●	●
HVSASS Cyclones	2					●	●	●	●	●	●	●
Coal	1			●	●	●	●	●	●	●	●	

*Locations as noted in Figure A-2.

was a 10-inch port which had a plate attached which reduced the port to a 4-inch male pipe fitting. There were also two 10-inch ports 180° with respect to each other and 45° from the 4-inch ports. The 4-inch ports were designated as the north, south, east and west ports. The 10-inch ports were designated as the north-west and south-east ports.

Velocity measurements were taken daily from the east and west ports using three points. These points were selected by dividing the cross-sectional area of the stack into three equal area concentric circles and determining the distance from the centroid of each circle to the inner stack wall as specified in EPA Method 1. The distances from the inner stack wall for the three points were:

- 1 foot 1 inch,
- 3 feet 6 inches, and
- 7 feet 1 inch.

The average velocity of the flue gas was 71 fps. The velocity traverses were used to determine the sampling rates necessary for isokinetic sampling and for the determination of total gas flow through the stack.

Particulate loading measurements were conducted on 7 days during the sampling of Station CS using in-stack Gelman filters. The grain loading measurements were conducted at the north-west port. Table A-4 contains the results of these measurements during the sampling period.

The moisture content of the stream was determined by condensation in a series of Smith-Greenburg impingers and then final drying in an impinger containing silica gel. The average moisture content of the flue gas was found to be 9.3%.

TABLE A-4. PARTICULATE LOADINGS AT STATION CS

Date	Grain Loading in gr/scf*
9/21/76	0.008
9/22/76	0.013
9/23/76	0.009
9/24/76	0.022
9/25/76	0.008
9/27/76	0.015
9/28/76	0.025
Mean ± std deviation	0.014 ± .007

*60°F, 1 ATM

3.3 Flow Rate Measurements

The following section describes the methods used to determine the flow rates of the individual streams at Station CS.

3.3.1 Coal

Coal is fed from the storage silos to the mills by a series of five feeders. The flow of the coal is measured in 100-pound units. The metering devices are located in the control room. Readings from the meters were taken at the beginning and end of each day of sampling. From these values the amount of coal fed to the boilers as a function of time was calculated. The coal feed rate of Unit 1 was determined to be 5.3×10^5 lb/hr.

3.3.2 Fly Ash Flow Rate

The flow rate of the flue gas was determined to be 1.9×10^6 ACFM using the average gas velocity of 71 fps and the cross-sectional area of the stack at the test plane. The fly ash flow rate was determined using the flue gas flow rate and the average grain loading. The average fly ash flow rate was calculated to be 1.3×10^2 lb/hr.

4.0 PARTICULATE COLLECTION BY SIZE FRACTIONS

Fly ash was collected by size fractions using three different sampling systems:

- Andersen cascade impactors,
- three one-acfm cyclones, and
- three five-acfm cyclones from the HVSASS train.

Each of these systems used a wet electrostatic precipitator (WEP) to collect the "less than" fraction escaping the primary collection device. The WEP is shown schematically in Figure A-3. Teflon-lined tubing carried the sample from the primary collection device to the WEP. The sample entered by bubbling through the electrolyte reservoir then passed up through a cylindrical chamber, the walls of which were wetted by the circulating electrolyte. Collection of fine particulate was achieved in this area by the 12 KVDC potential between the electrolyte and the center platinum electrode which induces electrostatic collection. The circulating electrolyte for the WEP was 5% sulfuric acid. The gas stream then exited the device and continued to a series of impingers containing 6% hydrogen peroxide and silica gel for the removal of corrosive gases and moisture. Upon completion, the sample which includes both the fine particualtes and vapor phase elements collected by the WEP is contained in the electrolyte.

The remainder of this section describes the three primary collection techniques used to collect particulate by size fractions.

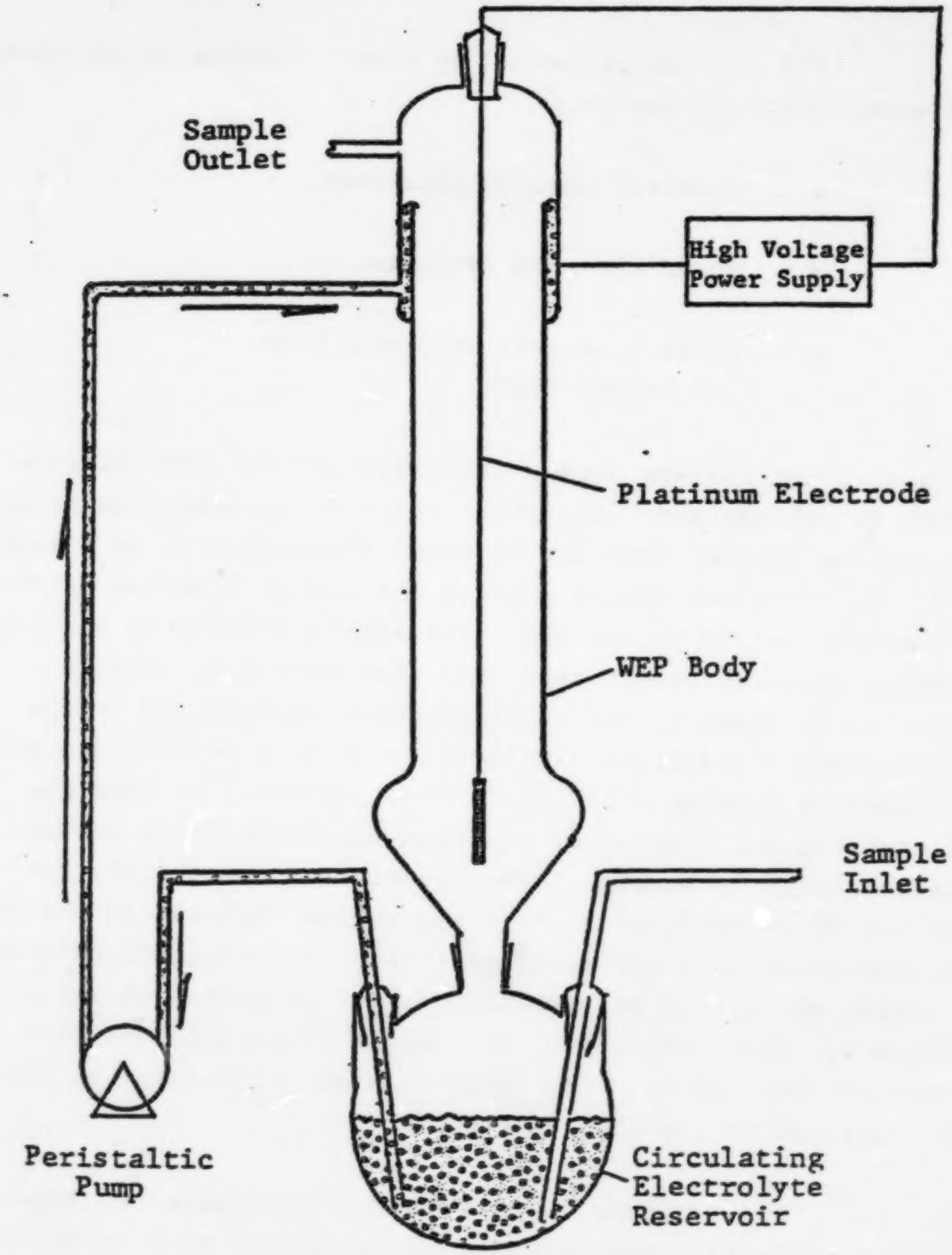
Sample Outlet
High Voltage Power Supply
Platinum Electrode
WEP Body
Sample Inlet
Peristaltic Pump
Circulating Electrolyte Reservoir

Figure A-3. Wet Electrostatic Precipitator (WEP)

4.1 Andersen Cascade Impactors

Particulate entrained in the flue gas was separated into nine size fractions by an Andersen cascade impactor. This device is shown schematically in Figure A-4. The Andersen aerodynamically separates the fly ash particles into size fractions as they pass through a series of multi-jet stages. Fine particulates passing through the last impactor stage enter the previously described WEP via a teflon-lined probe and teflon tubing.

During sampling, two Andersen/WEP trains were run simultaneously. Tables A-5 and A-6 present the sample quantities collected at each stage with the Andersens at the two stations.

4.2 One-acfm Cyclones

A series of three cyclones were used in-stack to collect fly ash in four size fractions. The cyclones were designed to operate at a flow rate of one actual cubic foot per minute and have D_{50}'s of 2.65μ, 0.96μ and 0.60μ. They are constructed of 7075 T6 alloy aluminum and black anodized to minimize corrosion. The cyclones were used in-stack and clustered to minimize losses onto the walls of interconnecting tubing.

The "less than" fraction escaping the last cyclone was carried to a WEP via a teflon-lined probe and teflon tubing. Following collection by the WEP, the gas stream entered a series of impingers to remove moisture, then passed through a leakless pump and dry gas meter. Particulate which lodged in the probe was rinsed into the WEP. A summary of particulate collected using the one-acfm cyclones is given in Tables A-7 and A-8.

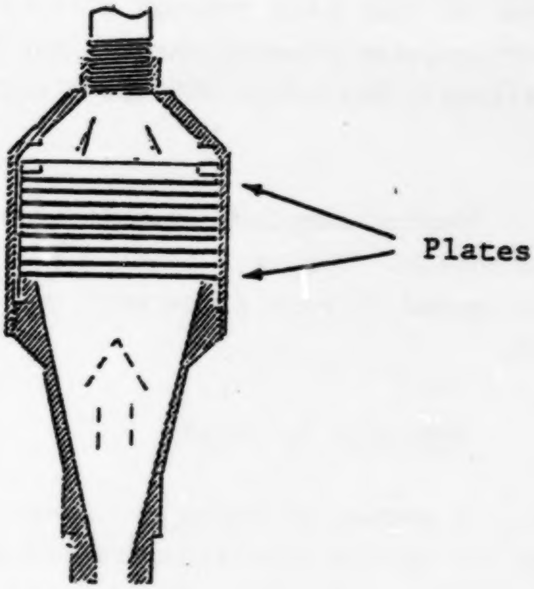

Figure A-4. Andersen Mark III Cascade Impactor

TABLE A-5. SUMMARY OF DATA FOR PARTICULATE COLLECTION BY ANDERSEN CASCADE IMPACTOR AT STATION HS

Stage	Size Range in μ	Total Weight Collected in g	% Fly Ash Distribution
1	>8.0	0.741	9.4
2	5.0-8.0	0.892	11.4
3	3.3-5.0	1.300	16.6
4	2.3-3.3	0.908	11.6
5	1.5-2.3	1.635	20.9
6	0.74-1.5	1.344	17.2
7	0.45-0.74	0.675	8.6
8	0.30-0.45	0.214	2.7
	Total Weight Collected by Andersen	7.709	98.4
	Total Volume Sampled - 1665 SCF		
	Ave. Flow Rate - .78 ACFM		
WEP	<.3	(0.122)*	1.6
	Total Weight Collected by WEP - .0352g		
	Total Volume Sampled - 479 SCF		
Total Particulate Catch		7.831	100%

Grain Loading - .073 gr/SCF

---

* Effective particulate collected by WEP for 1665 SCF.

TABLE A-6. SUMMARY OF DATA FOR PARTICULATE COLLECTION BY ANDERSEN CASCADE IMPACTOR AT STATION CS

Stage	Size Range in μ	Total Weight Collected in g	% Fly Ash Distribution
1	>8.2	0.851	15.3
2	5.1-8.2	0.375	6.8
3	3.4-5.1	0.559	10.1
4	2.4-3.4	0.575	10.4
5	1.5-2.4	0.923	16.6
6	0.77-1.5	1.207	21.8
7	0.47-0.77	0.732	13.2
8	0.32-0.47	0.137	2.5
	Total Weight Collected by Andersen	5.360	96.7%
	Total Volume Sampled - 4158 SCF		
	Ave. Flow Rate - .67 ACFM		
WEP	<.32	(0.183)*	3.3
	Total Weight Collected by WEP - .0466g		
	Total Volume Sampled - 1059 SCF		
Total Partiuclate Catch		5.543	100%

Grain Loading - .021 gr/SCF

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* Effective particulate collected by WEP for 4158 SCF.

TABLE A-7. SUMMARY OF DATA FOR PARTICULATE COLLECTION WITH ONE ACFM CYCLONES AT STATION HS

Unit	Size Range in μ	Total Weight Collected in g
Cyclone 1	>2.65	5.123
Cyclone 2	2.65-0.96	2.713
Cyclone 3	0.96-0.60	2.183
WEP	<0.60	---

Total weight collected by cyclones - 10.019g

Total volume sampled - 1250 scf

TABLE A-8. SUMMARY OF DATA FOR PARTICULATE COLLECTION WITH ONE ACFM CYCLONES AT STATION CS

Unit	Size Range in μ	Total Weight Collected in g
Cyclone 1	>2.65	2.325
Cyclone 2	2.65-0.96	1.245
Cyclone 3	0.96-0.60	0.444
WEP	<0.60	---

Total weight collected by cyclones - 4.014g

Total volume sampled - 3022.05 scf

4.3 HVSASS Cyclones

The three cyclones from the High-Volume Source Assessment Sampling System train were used to collect particulate by size fractions. The train consisted of a nozzle, 5-foot probe, and a heated oven containing three cyclones designed to operate at 4 standard cubic feet per minute. The glass fiber back-up filter normally used with the HVSASS train was removed for this study. The flow leaving the smallest cyclone was diverted to a tee. Approximately one-fifth of the gas stream was routed to a WEP and the remainder into the series of high-volume impingers which are normally used with the HVSASS. These impingers contained a 6% solution of hydrogen peroxide. The sampling train as used in this study is shown in Figure A-5.

During sampling, the temperature of the cyclones was held at 400°F. The particulate was collected in four size fractions. Three were contained in the cyclones and the fourth, the "less than" fraction, was collected by the WEP. However, due to the flow rate limitation of the WEP, only part of the gas stream was passed through the WEP. The D_{50}'s of the HVSASS cyclones were established prior to sampling to be 14μ, 4μ and 1μ. The weight of material collected in each of the cyclones is summarized in Tables A-9 and A-10.

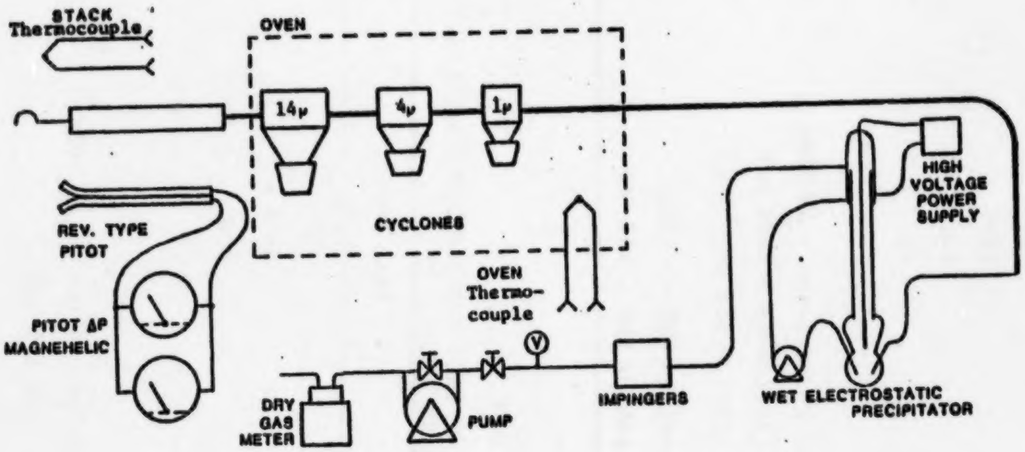

STACK Thermocouple
OVEN
14μ
4μ
1μ
CYCLONES
REV. TYPE PITOT
PITOT ΔP MAGNEHELIC
OVEN Thermo-couple
HIGH VOLTAGE POWER SUPPLY
DRY GAS METER
PUMP
IMPINGERS
WET ELECTROSTATIC PRECIPITATOR

Figure A-5. Schematic of Sampling Train for Particulate Sizing with HVSASS Cyclones

TABLE A-9. SUMMARY OF DATA FOR PARTICULATE COLLECTION WITH THE HVSASS CYCLONES AT STATION HS

Unit	Size Range in μ	Total Weight Collected in g
Cyclone 1	>14	5.359
Cyclone 2	14-4	7.399
Cyclone 3	4-1	5.526
WEP	<1	(0.986)*

Total weight collected by cyclones - 18.284g

Total volume sampled (cyclones) - 2920 scf

Total volume sampled (WEP) - 571 scf

* Total weight collected by WEP - .159g

Total volume collected by WEP - 471 SCF

TABLE A-10. SUMMARY OF DATA FOR PARTICULATE COLLECTION WITH HVSASS CYCLONES AT STATION CS

Unit	Size Range in μ	Total Weight Collected in g
Cyclone 1	>14	2.870
Cyclone 2	14-4	5.949
Cyclone 3	4-1	8.943
WEP	<1	(3.647)*

Total weight collected by cyclones - 17.762g

Total volume sampled - 12,540 scf

* Total weight collected by WEP - .260g

Total volume collected by WEP - 894 SCF

APPENDIX B

ANALYTICAL PROCEDURES

1.0 INTRODUCTION

Trace element analyses on coal and ash samples from the two coal-fired power plants were performed using dissolution and analytical techniques adapted specifically for these matrices. The following sections provide brief descriptions of the sample preparation and analytical procedures for:

Arsenic
Beryllium
Cadmium
Calcium
Copper
Chromium
Fluorine
Lead
Manganese
Mercury
Nickel
Selenium
Titanium
Uranium
Zinc

2.0 INSTRUMENTATION

The following instrumentation was utilized in the analysis of the samples at the Radian trace analysis laboratories:

- Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer,
- Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer,
- Perkin-Elmer Model HGA 200 Heated Graphite Analyzer,
- Instrumentation Laboratory Model 351 Atomic Absorption Spectrophotometer,
- Instrumentation Laboratory Model 555 Flameless Atomizer,
- Perkin-Elmer Model 124 Double Beam Spectrophotometer,
- Turner III Fluorometer,
- International Plasma Corp. Model 1001 Low Temperature Asher, and
- ETEC Scanning Electron, Microscope with PGT 1000 Energy Dispersive X-Ray Detector.

3.0 SAMPLE PREPARATION

Preparation procedures were performed on the following types of samples to provide the primary analytical solution:

- coal,
- coal ash, and
- WEP (solids).

3.1 Coal

Perchloric Acid Digestion (PAD)

For the trace element analysis of coal, Radian combined low-temperature ashing with a perchloric acid digestion procedure suggested by Theodore Rains (DE-218) of the National Bureau of Standards.

The coal samples are ashed in 1-gram portions in a low-temperature asher. Dissolution is achieved by a three-step acid treatment using the following ultrex grade acids:

- nitric acid,
- a 2:1:1 mixture of nitric, hydrochloric and hydrofluoric acids, and
- perchloric acid.

Lithium Metaborate Fusion

A lithium metaborate fusion procedure reported by Boar and Ingram (BO-028) is used for the analysis of the major constituents of coal.

Coal which has been previously ashed is thoroughly mixed with lithium metaborate in a platinum crucible and fused at 1050°C for 15 minutes. The flux is cooled and then dissolved using hydrochloric acid and water.

3.2 Ash

Perchloric Acid Digestion (PAD)

The ash is weighed into a Teflon beaker and digested using the same dissolution procedure used for the coal.

Lithium Metaborate Fusion

The ash is fused using the same procedure used for the coal.

3.3 WEP

The solids are filtered from the WEP solution using a 0.8μ cellulose membrane filter. The solids and the filter are digested using the perchloric acid digestion procedure and are added back to the filtrate.

4.0 ANALYTICAL PROCEDURES

The analytical techniques used were developed for trace element determinations in coal, coal ash and WEP samples. Each analytical technique has been screened for accuracy and reliability by standard addition and interference studies. NBS coal (SRM 1632) and fly ash (SRM 1633) standards were analyzed with the samples to check analytical techniques.

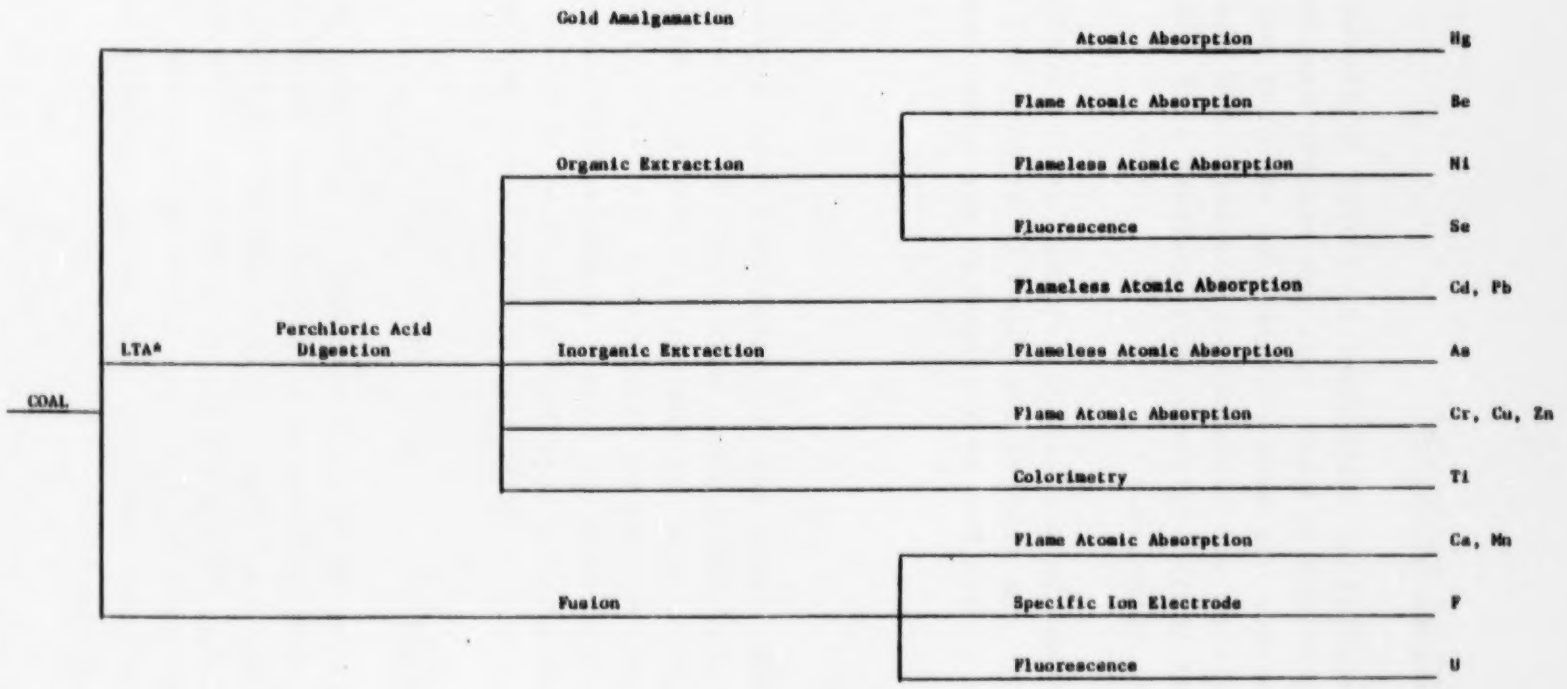
The complete analytical schemes for the analysis of trace elements in the samples are found in Figures B-1 through B-3. Detection limits for each procedure are summarized in Table B-1.

Arsenic

The WEP liquor and the perchloric acid digestion of the solids are used for arsenic determination. Arsenic is complexed, in acidic medium, as the heteropolyacid of molybdenum using the method proposed by Ramakrishna (RA-147). The aqueous complex is injected into the heated graphite analyzer attachment to the atomic absorption spectrophotometer at 193.7 nm. A charring temperature of 1200°C is used to remove any interferences.

Beryllium

Beryllium in aqueous solution is complexed with 2,4-pentanedione. Ethylenediaminetetraacetic acid (EDTA) is used to mask interfering ions. The beryllium complex is extracted into methyl-isobutyl-ketone (MIBK) and aspirated into the nitrous oxide-acetylene flame of the AA at 234.9 nm according to a procedure by Bokowski (BO-027). The perchloric acid digestion is used for solid samples.


Gold Amalgamation
Atomic Absorption
Hg
Flame Atomic Absorption
Be
Organic Extraction
Flameless Atomic Absorption
Ni
Fluorescence
Se
Flameless Atomic Absorption
Cd, Pb
LTA*
Perchloric Acid Digestion
Inorganic Extraction
Flameless Atomic Absorption
As
COAL
Flame Atomic Absorption
Cr, Cu, Zn
Colorimetry
Ti
Flame Atomic Absorption
Ca, Mn
Fusion
Specific Ion Electrode
F
Fluorescence
U

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*LTA - Low Temperature Asher

Figure B-1. Analytical Flow Chart for Coal Samples

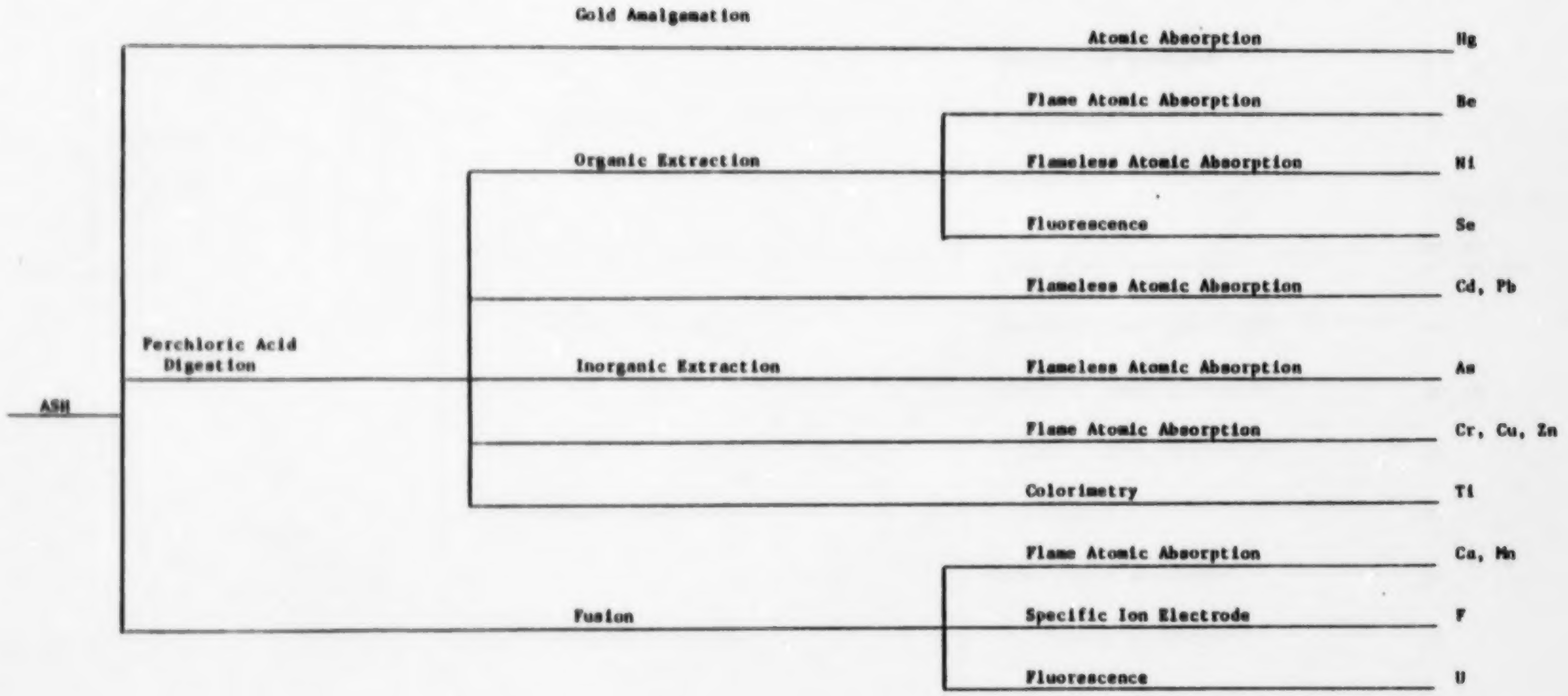
Gold Amalgamation
Atomic Absorption
Hg
Flame Atomic Absorption
Be
Organic Extraction
Flameless Atomic Absorption
Ni
Fluorescence
Se
Flameless Atomic Absorption
Cd, Pb
Perchloric Acid
Digestion
Inorganic Extraction
Flameless Atomic Absorption
As
ASH
Flame Atomic Absorption
Cr, Cu, Zn
Colorimetry
Tl
Flame Atomic Absorption
Ca, Mn
Fusion
Specific Ion Electrode
F
Fluorescence
U

Figure B-2. Analytical Flow Chart for Ash Samples

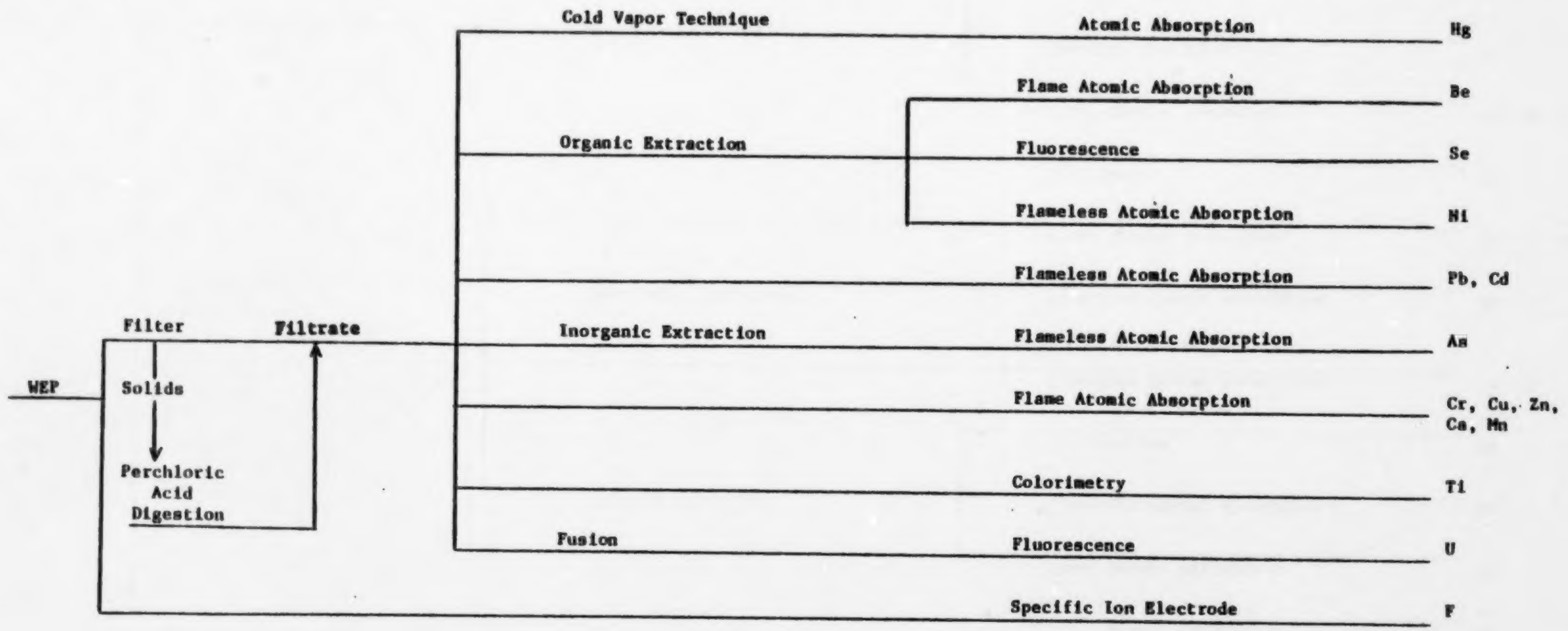
WEP
Filter
Solids
Perchloric
Acid
Digestion
Filtrate
Cold Vapor Technique
Atomic Absorption
Hg
Organic Extraction
Flame Atomic Absorption
Be
Fluorescence
Se
Flameless Atomic Absorption
Ni
Flameless Atomic Absorption
Pb, Cd
Inorganic Extraction
Flameless Atomic Absorption
As
Flame Atomic Absorption
Cr, Cu, Zn,
Ca, Mn
Colorimetry
Ti
Fusion
Fluorescence
U
Specific Ion Electrode
F

Figure B-3. Analytical Flow Chart for WEP Solution

TABLE B-1. DETECTION LIMITS FOR TRACE ELEMENT ANALYSIS

Element	Analytical Procedure	Detection Limit (ppm)		
		Coal	Ash	WEP
As	Atomic Absorption (AA)	0.1	0.5	0.001
Be	Extraction/AA	0.2	1.6	0.001
Ca	Atomic Absorption	10	40	0.1
Cd	Atomic Absorption	0.1	0.2	0.0002
Cr	Standard Addition/AA	10	25	0.1
Cu	Standard Addition/AA	1	4	0.1
F	Specific Ion Electrode	0.5	1.2	0.1
Hg	Cold-Vapor AA	0.01	0.01	0.0005
Mn	Atomic Absorption	10	40	0.01
Ni	Extraction/AA	2	8	0.006
Pb	Atomic Absorption	0.4	0.8	0.004
Se	Fluorometry	0.1	0.1	0.0005
Ti	Spectrophotometry	5	20	0.1
U	Fluorometry	0.0001	0.0001	0.0001
Zn	Atomic Absorption	1	4	0.01

Cadmium and Lead

The WEP solutions and the perchloric acid digestions of the solids are analyzed by direct injection into the graphite furnace attachment of the AA. Using Perkin-Elmer standard conditions (PE-082), cadmium absorbance is measured at 228.8 nm and lead at 283.3 nm.

Calcium and Manganese

The WEP solutions and the lithium metaborate fusions of the solids were analyzed by direct aspiration into the flame of the AA at 422.7 nm for calcium and at 279.5 nm for manganese under Perkin-Elmer standard conditions (PE-114). Species interfering with the calcium analysis are suppressed by aspirating a lanthanum chloride solution with the sample using double-capillary aspiration. Single-capillary aspiration is used for the manganese analysis.

Chromium, Copper and Zinc

Chromium, copper and zinc are determined by direct aspiration of the perchloric acid digestions and WEP solutions into the flame of the AA. Chromium and copper determinations are made by the use of standard additions with a double-capillary aspiration system at 357.9 nm and 324.7 nm, respectively. Zinc determinations are made by a single-capillary system at 213.9 nm. All are done under standard conditions (PE-114).

Fluorine

Baker (BA-131), Baumann (BA-137) and Thomas (TH-060) describe standard addition techniques utilizing a specific ion electrode for the measurement of fluorine. A citrate buffer is added to release fluoride complexed by uranium, thorium, aluminum and iron and to cancel out variances in pH and ionic strength. The observed potential changes can then be related directly to fluoride concentration.

Solid samples are fused with sodium carbonate at 600°C and the melt is extracted with hot water. After diluting the extract to volume, an aliquot is neutralized with acetic acid before analysis.

Mercury

Mercury in gaseous and solid samples is determined using a double gold amalgamation procedures described by Kalb and Baldeck (KA-086), Diehl, Haltman, Schultz and Haven (DI-043), and O'Gorman, Suhr and Walker (OG-004).

Gas samples are drawn through a plug of gold wool. Deamalgamation is accomplished by heating the gold wool with a nichrome wire heating element. The released mercury is purged through the absorption cell of an atomic absorption spectrophotometer (AA) at 253.7 nm.

Solid samples are analyzed for mercury by weighing a sample into a platinum boat and heating the sample slowly in a chamber. The off gases containing elemental mercury are purged through a gold plug where the mercury is collected. Deamalgamation and determination by AA follow the same procedure as described above.

Mercury in the WEP was determined by the procedure of Hatch and Ott (HA-087). Liquid samples are acidified and the mercury oxidized with potassium permanganate. Hydroxylamine hydrochloride and stannous choride are used to reduce the mercury to the metallic state. Air is bubbled through the solution. The mercury-entrained air is passed through the absorption cell of an AA at 253.7 nm.

Nickel

Joyner, Healy, Chakravarti and Koyanagi (JO-012) report a procedure using diethyldithiocarbamate to chelate nickel for extraction into MIBK. The organic extract is injected into the graphite furnace attachment of the AA at 232.0 nm. Nickel is extracted from the WEP liquor and perchloric acid digestion of the solids.

Selenium

Selenium is determined by a fluorescence method reported by Levesque and Vendette (LE-068), Rankin (RA-082), and an instrument firm, Turner Associates (TU-082). WEP liquors and perchloric acid digestions are heated with hydrochloric acid. Following stabilization with formic acid, hydroxylamine hydrochloride and EDTA, the samples are complexed with 2,3-diaminonaphthalene. The selenium complex is extracted into cyclohexane and compared by fluorometry with extracted selenium standards.

Titanium

The perchloric acid digestions and WEP Solutions are used for the titanium analysis. A yellow complex of titanium is formed with tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate) and read at 430 nm with a spectrophotometer using a method by Rader and Grimaldi (RA-125). Interference from ferric iron is eliminated by adding sodium dithionate.

Uranium

Uranium is determined at nanogram levels by fluorescence. Solid samples are mixed with a sodium carbonate, potassium carbonate and sodium fluoride flux mixture in a platinum crucible and fused into a translucent disc at 650°C. WEP solutions are evaporated to dryness in platinum crucibles and the residue fused with the flux. The fluorescence is measured with a Turner filter fluorometer (TU-025). The method of standard additions is used to compensate for quenching.

5.0 Analysis of Standard Reference Materials

The analytical techniques described were applied to NBS samples of Coal (SRM 1632 and Fly Ash 1633). The analytical results for triplicate analysis are presented in Table B-2 for comparison with certified values. In instances where certified values were not available the results of Ondov (ON-22) were substituted for comparison. No reported values for fluorine were identified.

TABLE B-2. ANALYSIS OF NBS STANDARD REFERENCE MATERIALS

Element	Coal NBS 1632		Fly Ash NBS 1633	
	Results	Reported Value	Results	Reported Value
As	6.4 ± .9	5.9 ± .6	82 ± 8	61 ± 6
Be	1.4 ± .1	∿1.5	9.5 ± 1.3	∿12
Ca	.37 ± .02%*	.43 ± .05%	4.9 ± .4	4.7 ± 6%*
Cd	.17 ± .04	.19 ± .03	1.6 ± .2	1.45 ± .06
Cr	21 ± 2	20.2 ± .5	125 ± 8	131 ± 2
Cu	22 ± 3	18 ± 2	126 ± 9	128 ± 5
F	76 ± 8	NR	180 ± 25	NR
Hg	.14 ± .03	.12 ± .02	.16 ± .03	.14 ± .01
Mn	45 ± 4	40 ± 3	530 ± 30	493 ± 7
Ni	14 ± 1	15 ± 1	89 ± 6	98 ± 3
Pb	24 ± 7	30 ± 9	75 ± 9	70 ± 4
Se	3.1 ± .3	2.9 ± .3	9.5 ± 1.0	9.4 ± .5
Ti	1000 ± 100	1040 ± 110	7200 ± 300	7400 ± 300
U	1.5 ± .1	1.41 ± 0.7	12.7 ± 1.4	12.0 ± .5
Zn	38 ± 5	37 ± 4	210 ± 15	210 ± 20

All values in ppm (μg/g) unless otherwise indicated.
Results are for triplicate digestions of each standard.
*Source ON-022 (not certified by NBS).
NR - Not Reported.

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